

CHAPTER VI

PREPARATION AND CHARACTERIZATION OF EXFOLIATED GRAPHENE OXIDE (eGO)

Chapter Overview

Graphene oxide, the single-sheet form of graphene with oxygen-containing moieties, can be prepared as a colloid by the exfoliation of graphite oxide in water. Historically, graphite oxide has been produced by the treatment of graphite with a combination of a concentrated acid and a strong oxidizer. Several of these methods are described in reference [60]. In recent studies, the Hummers method, using sulfuric acid and potassium permanganate, has been scaled down for bench-top work. (Hummers' report prescribed the treatment of 100 g graphite in a 15 L battery jar!) This chapter details the synthesis and characterization of the exfoliated graphene oxide (eGO) as well its suspensions in water.

6.1 Synthesis

Graphite oxide was prepared from graphite using the modified Hummers method [61]. Bay Carbon, Inc., provided a sample of graphite (catalog item SP-1, powder, shown in Figure 6-1). All other reagents were purchased from Sigma Aldrich. In a round-bottom flask, 2 g graphite and 50 ml H_2SO_4 were combined. The flask was placed in an ice water bath, with a stir bar set to 500 rpm. Once the temperature inside the flask reached 1 °C, 7 g of KMnO_4 powder was added in 1 g increments, causing the flask contents to turn a dark green color. The flask was removed from the ice bath and brought to 35 °C by using a silicone oil bath. (In the reference, the rate at which to raise the temperature to 35 °C was not specified, so we erred on the side of caution by allowing the contents to rise to 32 °C by the reaction itself, then adding the oil bath to bring the contents to the specified 35 °C. This entire process took 60 min.) As specified in the modified method, the reaction was run for 120 min at this temperature. At the end of 120 min, the contents of the flask appeared as a dark brown sludge.

The first step of quenching the reaction was to return the flask to the ice bath. The flask contents were diluted by the addition of 100 ml of deionized water that had been held in the ice water bath for ~ 20 min. To consume any unreacted permanganate ion, refrigerated H₂O₂ was added in 10 ml increments. After 30 ml H₂O₂ were added, the temperature of the contents rapidly rose to ~ 95 °C, accompanied by intense bubbling (evolution of steam and oxygen gas) and a change in color of the suspension to yellow. A further 15 ml H₂O₂ were added, after which bubbling subsided. The contents of the flask were poured into a glass filter. Filtration yielded a chunky, moist brown powder, the graphite oxide product. The product was washed with a dilute HCl solution (10% in water) to remove sulfates that could have precipitated on the product. The product remained moist even after overnight drying in the vacuum filtration setup.

Accurate measurement of the graphite oxide powder's mass for subsequent preparation of suspensions required the powder to be dry. To remove the moisture from the graphite oxide, the chunky powder was freeze-dried using a Labconco FreeZone Plus 2.5. Overnight treatment in this instrument yielded a dry powder (Figure 6-1).

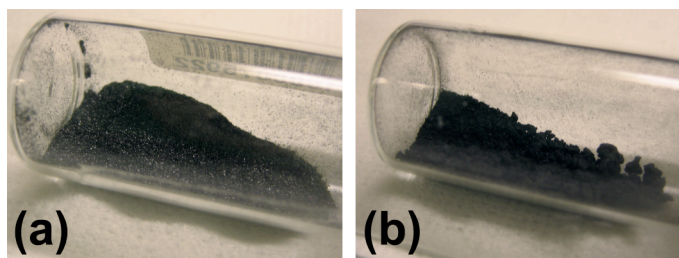


Figure 6-1. Photographs of (a) the precursor graphite powder and (b) the freeze-dried graphite oxide powder.

6.2 Chemical Characterization

This section details the chemical characterization of the synthesized eGO sheets. Ultraviolet-visible (UV-Vis) spectroscopy and Raman spectroscopy suggested a loss of electronic conjugation in the sp²-hybridized carbon graphitic network, while X-ray photoelectron spectroscopy (XPS) and infrared (IR) spectroscopy provided insight about the chemical moieties

present on the eGO sheets. Thermogravimetric analysis (TGA) suggested the presence of adsorbed water on the eGO.

6.2.1 UV-Vis Spectroscopy

The eGO sheets were dispersed in deionized water (concentration 0.5 mg/ml), yielding a yellowish brown suspension. The UV-Vis absorbance spectrum was recorded using a Varian Cary 5000 UV-Vis-NIR spectrophotometer. A spectrum for plain water was taken as a background before scanning the eGO dispersion. The spectrum for eGO, shown in Figure 6-2, exhibits a peak at ~ 230 nm, which is in agreement with previous reports on graphene oxide [62].

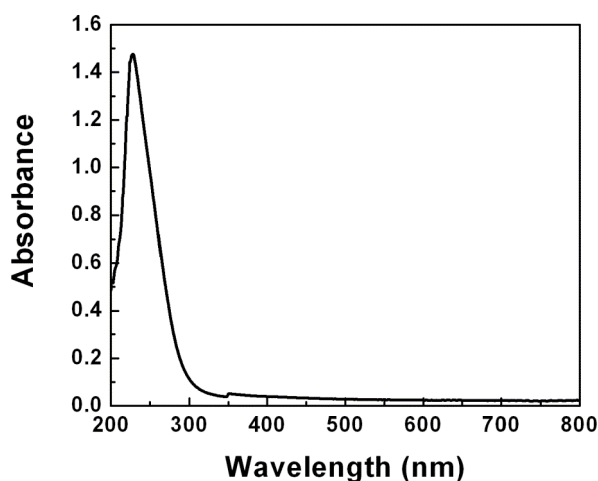


Figure 6-2. UV-Vis absorbance spectrum for exfoliated graphene oxide sheets.

In a conjugated system (a compound with alternating single and double bonds between carbon atoms), which is characterized by a delocalized electron environment, electronic transitions generally are of π -bonding electrons to the π^* antibonding orbital. The greater the extent of conjugation, the lower the energy that is needed for the π to π^* transition. The starting material, graphite, appears black because it absorbs photons through the entire visible spectrum down to relatively low-energy (high-wavelength) photons in the infrared. The lighter color of the

eGO, with its associated absorbance wavelength corresponding to higher-energy photons, can be attributed to the decrease in electronic conjugation resulting from the oxidation reaction.

6.2.2 Raman Spectroscopy

For Raman spectroscopy, we prepared samples on Au substrates. The eGO was drop cast from a 0.5 mg/ml suspension in water. The graphite precursor did not form a suspension in water, but by placing it in a vial of water and agitating the mixture, we were able to suspend a few grains of the powder momentarily and drop cast those onto the Au substrate. The Raman measurements were performed by Jed Ziegler in the group of Professor Richard Haglund using a scanning near-field optical microscope with a 532-nm laser.

The Raman shift spectra for both the graphite precursor and the eGO are shown in Figure 6-3. The graphite spectrum exhibited a peak at 1594 cm^{-1} (designated the G band), which corresponded to the stretching of the C–C bond in sp^2 -hybridized carbon [63]. In the eGO spectrum, the G band (now at 1603 cm^{-1}) appeared along with a new peak at 1374 cm^{-1} , which corresponded to the D band originating from phonon scattering at defect sites in the sp^2 carbon network [18, 63]. The origin of a broad shoulder at $\sim 1800\text{ cm}^{-1}$ in the eGO data could not be pinpointed to any carbon modes; it could have originated from residual solvent in the sample. The emergence of the D band further confirmed that our synthesis converted the graphite to a material containing both sp^2 -hybridized carbon and unconjugated carbon.

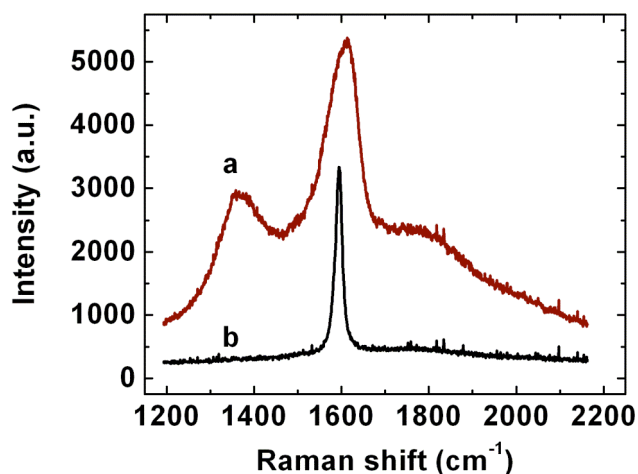


Figure 6-3. Spectra of Raman shift for (a) eGO and (b) graphite precursor. The peak locations are (a) 1374 cm^{-1} and 1603 cm^{-1} and (b) 1594 cm^{-1} .

6.2.3 X-ray Photoelectron Spectroscopy

We probed the chemical bonding states in the graphite precursor and in the eGO using XPS. In XPS, samples are irradiated with soft X-rays. In this work, monochromatic Al $K\alpha$ x-rays ($1486,6\text{ eV}$) were used. Electrons absorbing energy from the photons are ejected from the material by the photoelectric effect. By measuring the kinetic energy of these electrons, it is possible to calculate their binding energies in the sample using Equation (6.1),

$$E_{\text{Binding}} = E_{\text{X-ray}} - (E_{\text{Kinetic}} + \Phi) \quad (6.1)$$

where $E_{\text{X-ray}}$ is the energy of the X-ray, E_{Kinetic} is the measured kinetic energy, and Φ is the work function of the analyzer. The software used for the analysis compensates for the work function [64], so essentially, the binding energy is the difference between the kinetic energy and the energy of the photons used for excitation. The binding energy of these electrons provides information for elemental identification and about the chemical bonding in the sample. In this

analysis, we examined the spectra for the inner shell (“core”) electrons of carbon and oxygen, and identified bonding states from shifts in these spectra.

The XPS measurements and data analysis were performed by Robert Harl in the group of Professor Bridget Rogers. Measurements were performed in a PHI 5000 VersaProbe XPS and the data were analyzed and fitted using the CasaXPS software package. The eGO sample was prepared as a drop cast film on a thermally grown, 100 nm thick SiO₂ film. Prior to drop casting the eGO, the SiO₂ was cleaned using a Piranha solution to minimize the presence of organic contaminants. The graphite precursor, being insoluble in the solvents available in our laboratory, was prepared instead by pressing the powder into a thin indium foil. Survey scans were collected for the range 0 to 1300 eV using pass energy of 187.85 eV. Region scans for O 1s and C 1s bonding were done using pass energy of 23.5 eV. The pass energy controls the energy resolution of the analyzer. Lower values of pass energy enable higher energy resolution measurements.

Figure 6-4 shows the entire spectra for both samples. As expected, the graphite precursor showed a signal for carbon. There was a hint of an oxygen signal, likely originating from impurities in the material. In the eGO spectrum, the signals for carbon and oxygen were readily identified. The spectrum for eGO also revealed the presence of sulfur. The sulfur was likely a remnant from the synthesis, which used sulfuric acid.

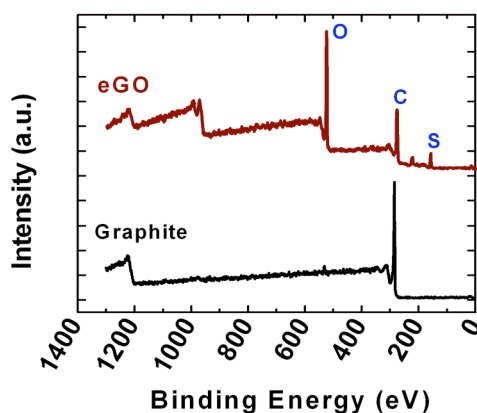


Figure 6-4. Spectra of XPS survey scans of graphite precursor and eGO.

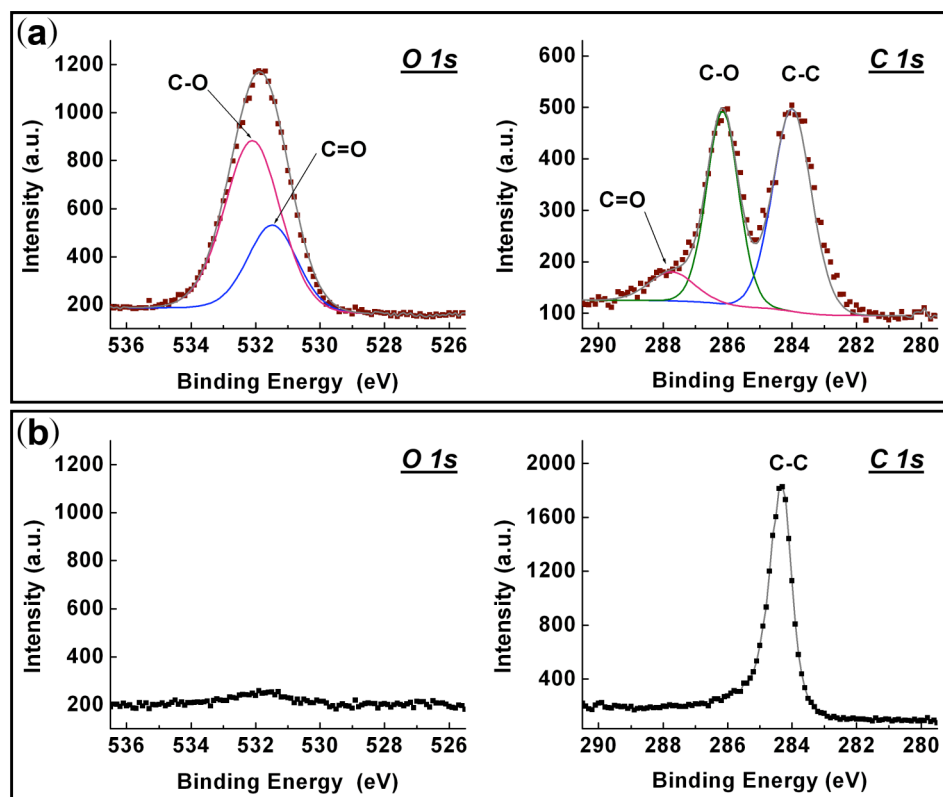


Figure 6-5. Spectra of O 1s and C 1s XPS region scans for (a) eGO and (b) graphite precursor.

Figure 6-5 shows the O 1s and C 1s region scans for both materials. The graphite scan exhibited a weak O 1s signal, in agreement with the survey scan. In the eGO scan there was a strong signal for O 1s bonding, which we attributed to C–O and C=O bonding. The contributions of different bonding states were fitted to the C 1s signal of each sample. In the graphite precursor, the signal originated from carbon atoms that are bonded to other carbon atoms. In the eGO, the signal originated from carbon atoms bonded to each other and to oxygen in C–O bonding and carbonyl bonding. The C–O bonding was indicative of epoxide (C–O–C) and/or hydroxyl (C–OH) groups bonded to the graphene sheet. Another group of researchers who studied eGO has argued that the carbon signal also contains contributions from carboxylate (O=C–O) bonding [65]. The XPS data presented here did not show a signal for carboxylate bonding. Further characterization, by IR spectroscopy, was needed to ascertain the presence of groups with carboxylate bonding.

6.2.4 Infrared Spectroscopy

We performed IR spectroscopy to determine whether the carbonyl bonding indicated by XPS corresponded to carboxylate groups. The graphite and eGO powders were prepared in KBr pellets for this measurement. Weidong He of the Dickerson group assisted in preparing the KBr pellet samples. Measurements were taken with a Bruker Tensor 27 FT-IR spectrometer. Figure 6-6 shows a segment of the IR spectra that would contain signals for stretching modes of carbonyl groups. The eGO spectrum contained peaks at 1577 cm^{-1} and 1615 cm^{-1} , which we attributed to deprotonated carboxylate ($\text{O}=\text{C}-\text{O}^-$) groups. The peak at 1723 cm^{-1} was attributed to aldehyde ($\text{O}=\text{C}-\text{H}$) groups, but the broadness of the peak suggested contributions as well from carboxylic acid (groups adjacent to unconjugated carbon networks (1710 cm^{-1})). The graphite spectrum contained weaker signals in the region shown, likely originating from the oxygen-containing impurities that XPS suggested. Given that UV-Vis absorbance and Raman spectroscopy already demonstrated the decreased level of conjugation in eGO, it would be reasonable to infer from the IR spectroscopy that the eGO contained groups with carboxylate bonding as well.

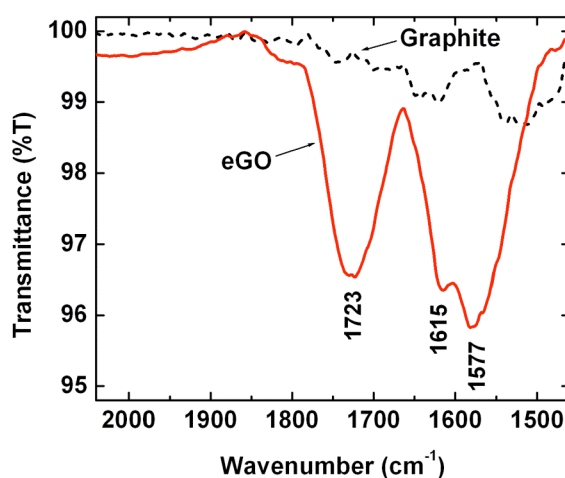


Figure 6-6. IR spectra examining carbonyl stretch modes of the graphite and eGO samples.

6.2.5 Thermogravimetric Analysis

TGA was performed on ~ 5 mg samples of the eGO (powder resulting from the freeze-drying step) and of the graphite precursor using a Scientific Systems TGA-1000 Analyzer. Suseela Somarajan of the Dickerson group configured the instrument for use and provided the raw data. The eGO sample was heated from 25 °C to 600 °C at a rate of 2.5 °C/min under nitrogen flow of 10 ml/min. (Initial TGA measurements of graphite and eGO were done at 15 °C/min as stipulated by VINSE scientist responsible for TGA instrument at the time.) The TGA data are shown in Figure 6-7. The graphite precursor exhibited minimal mass loss during the heating even with the relatively high heating rate of 15 °C/min. In the eGO samples, we anticipated mass loss due to the pyrolysis of oxygen-containing groups on the eGO, resulting in the evolution of steam, CO, and CO₂ gases [65]. The eGO sample heated at 15 °C/min exhibited a nearly complete mass loss at 200 °C caused by material flying out of the sample pan. The slower heating rate of 2.5 °C/min was necessary to measure mass loss without losing material from the pan because of rapid expansion from the gas evolution. When the eGO sample was heated at 2.5 °C/min, mass loss was observed throughout the heating. The mass loss below 100 °C was attributed to the loss of adsorbed water. Losses at higher temperatures were attributed to the decomposition of oxygen-containing groups. The presence of oxygen-containing groups on the eGO sheets promoted their interaction with water, which would be favorable for suspending the material in water to do electrophoretic deposition experiments.

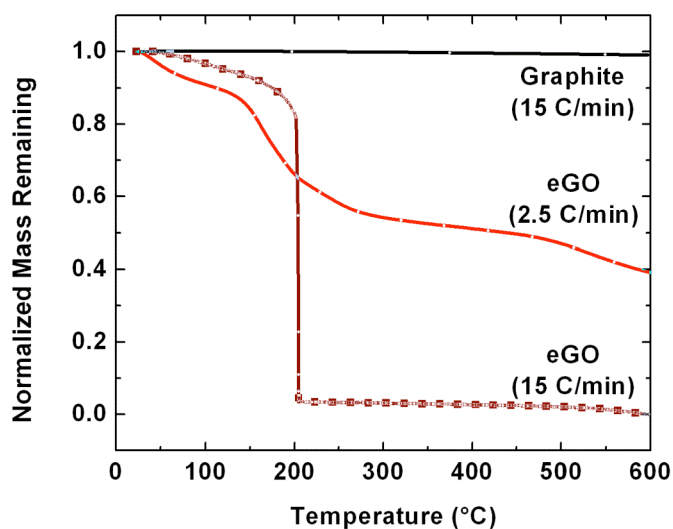


Figure 6-7. Normalized TGA plot for the graphite precursor and for the eGO powder product. The heating rate (°C/min) for each sample is indicated. The scatter point markers in the plot of eGO (15 °C/min) were added for visual clarity.

6.3 Structural Characterization

This section details the structural characterization of the eGO material. X-ray diffraction (XRD) measurements gave insight to the crystalline structure of the eGO sheets. Scanning electron microscopy (SEM) and atomic force microscopy (AFM) provided images of the sheet morphology.

6.3.1 X-ray Diffraction

The XRD measurements of the graphite precursor and the eGO powder were performed using a Scintag X1 powder x-ray diffractometer equipped with a Cu target ($\lambda = 1.5406 \text{ \AA}$) and a Peltier-cooled solid-state detector. The samples were supported on a zero-background Si (511) plate. Figure 6-8 shows XRD scans for both materials. The peaks indicated with Miller indices in the graphite precursor spectrum correspond to the standard graphite diffraction peaks (JCPDF # 41-1487). The smaller peaks likely originated from impurities in the material. Using Bragg's law ($\lambda = 2d \sin \theta$), we calculated the d-spacings associated with the indexed peaks in both samples.

Peak center locations and widths were determined from Gaussian fits to the original scan data. The peak locations and associated d-spacings for both spectra are listed in Table 6-1. These calculations formed the basis for comparing eGO's crystalline structure to that of the precursor material.

In the eGO spectrum, we observed peaks at 2θ values $\sim 26^\circ$ and $\sim 42^\circ$, in positions similar to the (0002) and $(10\bar{1}0)$ peaks, respectively, of the graphite precursor. We assigned the eGO peak at 42.73° to the $(10\bar{1}0)$ plane, which is reflective of an infinitesimal decrease in the d-spacing, from 0.213 nm to 0.211 nm. That this plane's d-spacing essentially remained constant is reasonable, given that the reaction of graphite to graphite oxide did not intend to alter the spacing between carbon atoms of the same graphene sheet. In contrast, the graphite (0002) peak at 26.50° was shifted to 25.87° , increasing the d-spacing from 0.336 nm to 0.344. An increase in this d-spacing was expected, since oxygen was added at the sheet edge and above the sheet surface. We assigned the secondary peak at 21.25° , corresponding to a d-spacing of 0.418 nm, to the (0002) plane as well. Previous studies of graphite oxide have reported d-spacings up to 1.2 nm, depending on the extent of oxidation and on the amount of adsorbed moisture in the inter-sheet space, which is a function of humidity level in the XRD chamber [65]. Our d-spacing measurement of 0.418 nm suggested that either our eGO material was not oxygenated to the maximum extent possible and/or the relative humidity in the XRD chamber was lower than that of researchers at other locations.

The eGO scan showed no evidence for the $(10\bar{1}1)$ and $(10\bar{1}2)$ peaks displayed in the graphite precursor scan. This is a reasonable observation, since the oxidation of the material altered the inter-sheet spacing in the $\langle 0001 \rangle$ direction. With varying separation in the $\langle 0001 \rangle$ direction, the regularity of the spacing for the $(10\bar{1}1)$ and $(10\bar{1}2)$ planes was eliminated. Thus, the XRD data for eGO corroborated the assertion from the chemical analyses that the eGO contained atoms in planar sheets bonded to oxygen-containing groups.

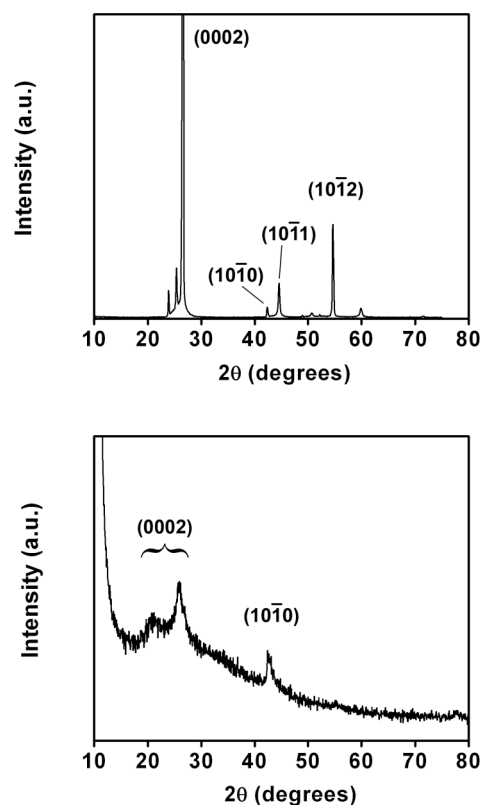


Figure 6-8. X-ray diffraction scans of (a) the graphite precursor and (b) the eGO sheets.

Table 6-1. X-ray diffraction peak positions and d-spacings: graphite precursor and eGO sheets.

| Lattice Plane | Peak Position (2θ degrees) | | d-spacing (nm) | |
|------------------|----------------------------|----------------|--------------------|----------------|
| | Graphite precursor | eGO | Graphite precursor | eGO |
| (0002) | 26.50 | 25.87 21.25 | 0.336 | 0.344 0.418 |
| (10 $\bar{1}$ 0) | 42.37 | 42.73 | 0.213 | 0.211 |
| (10 $\bar{1}$ 1) | 44.55 | No signal | 0.203 | N/A |
| (10 $\bar{1}$ 2) | 54.65 | No signal | 0.168 | N/A |

The broadening of the peaks in the eGO scan reflected the reduced size of crystalline grains compared to the graphite precursor. An analysis of the data for the (10 $\bar{1}$ 0) peaks using

the Scherrer equation indicated a decrease in the size of the crystalline domains within a single graphene sheet, from ~ 45 nm to ~ 10 nm. The addition of the oxygen-containing groups described in the previous section converted regions of the graphite to amorphous material, reducing the size of the crystalline regions. A neutron diffraction study of graphite oxide reported in the literature corroborates our observation that eGO is a nanocrystalline material, meaning it has crystalline domains interspersed with amorphous material [66].

6.3.2 Scanning Electron Microscopy

To get a first look at the morphology of eGO, we did SEM of the material after it had been washed and dried atop the filter post-synthesis. The imaging was performed with a Hitachi S-4200 microscope operating at 5 kV. Figure 6-9 shows the morphology of the material on the micron scale. Stacks of sheets, both flat and crumpled, appear in the images. This preparation and imaging, however, did not reveal isolated eGO sheets. In the next section, we describe an alternate approach to image single eGO sheets.

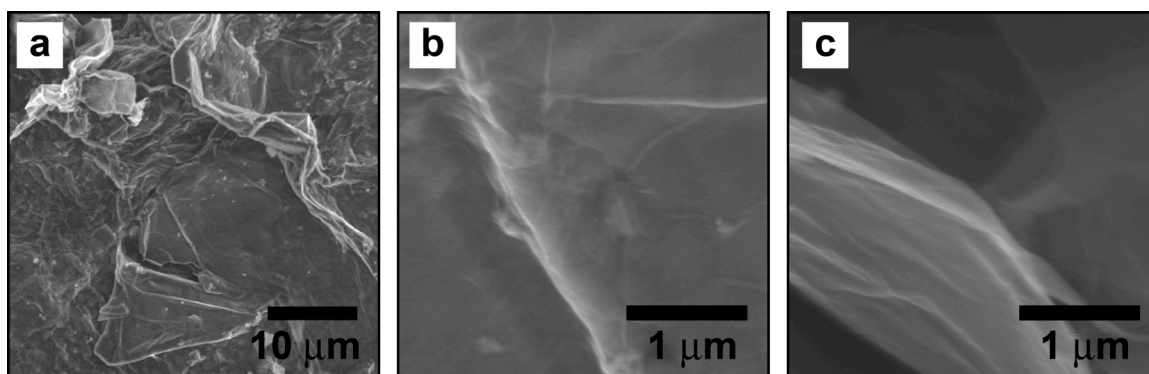


Figure 6-9. SEM images of the eGO material at (a) low and (b, c) high magnification.

6.3.3 Atomic Force Microscopy

We used AFM to verify if our synthesis and suspension preparation yielded single-layer sheets of graphene oxide. To prepare the material, a dilute suspension in water (0.35 mg/ml) was spun cast over a freshly exposed mica surface at 4,000 rpm for 60 s. John Rigueur of the

Dickerson group assisted with the mica preparation. Freshly exposed mica, prepared by Scotch tape separation, was selected for its atomically flat nature, which would aid in resolving the eGO sheets, expected to have sub-nanometer thickness. The high rotational velocity of the spin caster dispersed the sheets without aggregation, to enable imaging of individual sheets. The AFM scans were performed on a Digital Instruments Nanoscope III operating in tapping mode. The Nanoscope software was used to analyze the scan data.

The AFM scans of several eGO sheets are shown in Figure 6-10. The sheets are extremely thin and are characterized by varying lateral dimension on the order of hundreds of nanometers. Using the step-height calculator in the Nanoscope software, we were able to measure the thickness of the sheets. An example of how this was done appears in part (b) of Figure 6-10. We determined the eGO sheets to have thickness 0.65 ± 0.06 nm. Compared to the 0.34 nm thickness of a pristine graphene sheet, this value reflected the added oxygen atoms, present in groups such as epoxides above and below the plane of the original graphene sheet. An adsorbed layer of water above and/or below the sheets may have contributed to the measured thickness as well.

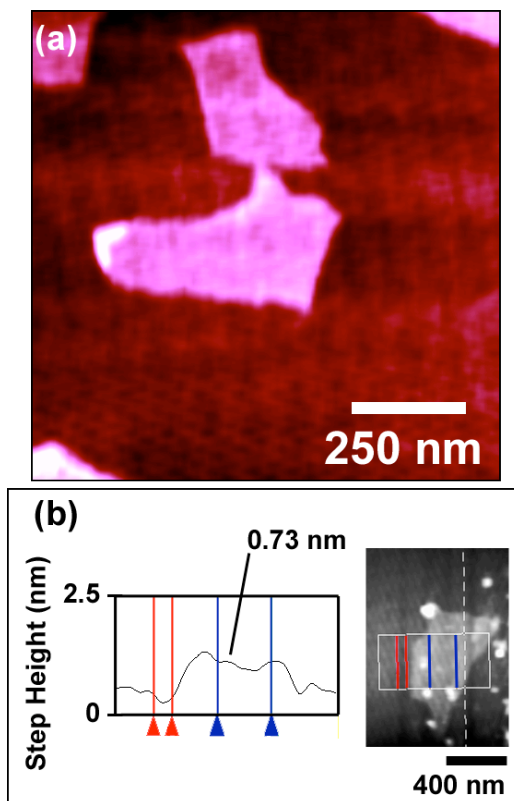


Figure 6-10. (a) AFM scan showing typical eGO sheets resting on freshly exposed mica surface. (b) Example of step height measurement on one eGO sheet.

6.4 Preparation and Characterization of eGO in Suspension

To investigate suspensions of eGO and perform electrophoretic deposition from them, we needed a protocol that minimized their variation from one preparation to the next. To this end, eGO powder was dispersed in deionized water at an initial concentration of 1.00 mg/ml. The powder and water were placed in a glass vial and sonicated for 120 min, yielding a brown suspension. From visual examination of the vial, we detected small aggregates that were not fully dispersed. To eliminate these aggregates from the suspension, it was lightly centrifuged using a Drucker 755VES. In a typical preparation, an 8 ml aliquot of the 1 mg/ml suspension was centrifuged for 5 min at 1000 rpm ($170 \times g$ rcf). The supernatant was isolated for further use. By freeze-drying the remnant pellet and taking its mass, we calculated the concentration of eGO in the supernatant suspension using Equations (6.2) and (6.3).

$$\text{Solid eGO mass in supernatant} = (8.00 \text{ mg}) \text{ minus (Mass of pellet)} \quad (6.2)$$

$$\text{Concentration of supernatant} = (\text{Solid eGO mass}) \text{ divided by (8.00 ml water)} \quad (6.3)$$

The supernatant eGO suspensions had a concentration of 0.92 ± 0.02 mg/ml. These suspensions were diluted to 0.35 mg/ml for characterization by dynamic light scattering (DLS) using the Malvern Zetasizer instrument. (DLS technique is explained in Appendix A.)

Using DLS, we established that the eGO sheets were characterized by hydrodynamic diameters in the range from 100 nm to 1,000 nm (Figure 6-11). The hydrodynamic diameter suggests the size of a spherical particle that would have the same diffusive behavior as the object being measured. The broad distribution of Figure 6-11, which corroborates the SEM and AFM imaging shown in the previous section, is reasonable given that no mechanisms were implemented to control the lateral size of the dispersed eGO sheets.

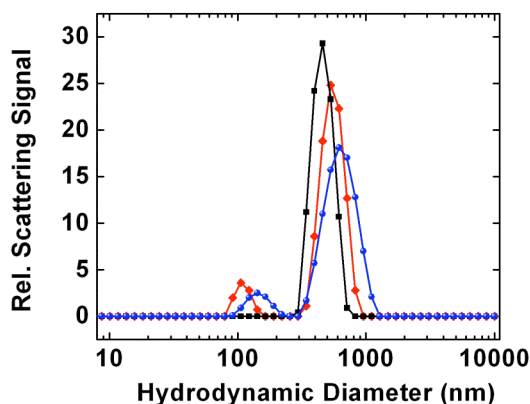


Figure 6-11. Dynamic light scattering measurements of eGO suspended in water. Each scan represents a different aliquot of the same suspension preparation.

6.5 Overall Picture of eGO

From the multifaceted characterization of the synthesized eGO material, we could portray it as a single graphene sheet, containing unconjugated regions, with epoxide and hydroxyl groups

attached above and below the plane of the carbon atoms and with carboxylate groups attached at the edges (Figure 6-12). The chemical characterization suggested the loss of conjugation and the addition of those oxygen-containing groups. The structural characterization indicated that the material was fully exfoliated into single sheets and that these sheets had lateral dimensions in the range 100 nm to 1,000 nm. The assignment of epoxide and hydroxyl groups to the planar surface and carboxylate groups to the sheet edges was based on the work of Lerf and Klinowski [67], who used solid-state NMR measurements to ascertain the locations of each group.

For eGO suspended in water, we anticipated that the carboxylate groups would be deprotonated to yield negatively charged (COO^-) moieties. The resulting colloids would therefore possess a negative zeta potential. The localization of negative charge on the sheet edges due to the position of the carboxylate groups could have important consequences on the shape of the electric double layer around the sheet. In aqueous suspensions, the double layer would be thin compared to the lateral dimension of the sheet, suggesting the use of the Smoluchowski approximation to calculate the zeta potential magnitude from an electrophoretic mobility measurement. The suspension behavior of the eGO sheets was tested in a series of experiments by tuning the pH of the eGO suspensions. The findings of these experiments are described in the next chapter.

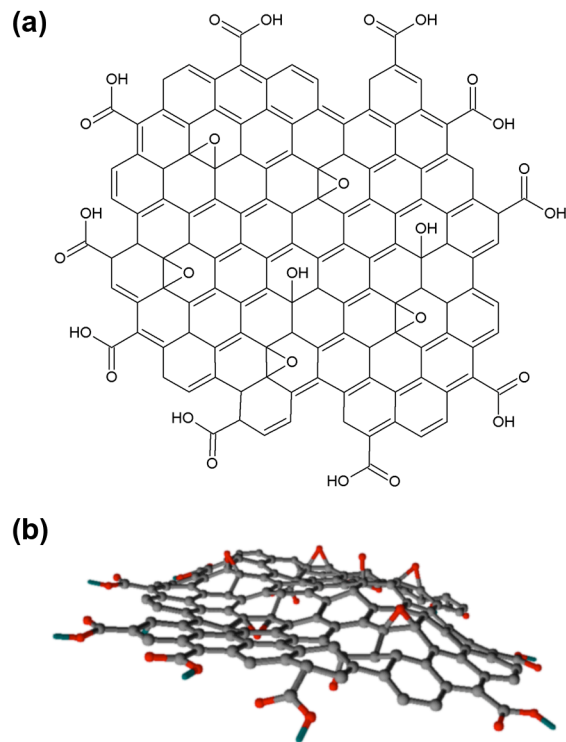


Figure 6-12. (a) Chemical structure and (b) 3-dimensional representation of an exfoliated graphene oxide sheet, showing relative position of oxygen-containing groups.