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Graphene Oxide: Synthesis, Characterization, Electronic Structure, and Applications

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Abstract. While graphite oxide was first identified in 1855 [1,2], the recent discovery of stable graphene sheets has led to renewed interest in the chemical structure and potential applications of graphene oxide sheets. These structures have several physical properties that could aid in the large scale development of a graphene electronics industry. Depending on the degree of oxidization, graphene oxide layers can be either semiconducting or insulating and provide an important complement to metallic graphene layers. In addition, the electronic and optical properties of these films can be controlled by the selective removal or addition of oxygen. For example, selective oxidation of graphene sheets could lead to electronic circuit fabrication on the scale of a single atomic layer. Graphene oxide is also dispersible in water and other solvents and this provides a facile route for graphene deposition on a wide range of substrates for macroelectronics applications. Although graphite oxide has been known for roughly 150 years, key questions remain in regards to its chemical structure, electronic properties, and fabrication. Answering these issues has taken on special urgency with the development of graphene electronics. In this chapter, we will provide an overview of the field with special focus on synthesis, characterization, and first principles analysis of bonding and electronic structures. Finally, we will also address some of the most promising applications for graphene oxide in electronics and other industries.

1.1 Introduction

The recent discovery that individual honeycomb atomic sheets of carbon or graphene could be easily isolated from bulk graphite with a bit of Scotch tape and persistence [3] has led to a flurry of research that has revealed unique electrical, thermal, and structural properties. While historically there are several instances where graphene was observed prior to 2004 [4], the recent synergy of nanoscale fabrication approaches with atomic scale characterization tools has provided the necessary environment to fully explore the potential of this material. In particular, for potential future electronic devices, graphene could provide a route to make truly atomic-scale electronic circuits by simply patterning an atomic layer of carbon into nanoribbons of various sizes and configurations. While the high electrical conductivity of graphene makes it a strong candidate for nanoscale electronics, graphene does not have the normal semiconducting properties that are usually required for key electronic devices such as field effect transistors and resonant tunneling diodes. Therefore, a considerable amount of work has focused on inducing a band gap in graphene nanoribbons [5], functionalized graphene, graphene bilayers [6] or else by integrating graphene with insulating atomic sheets such as hexagonal boron nitride [7].

In recent years, significant effort has also been devoted to finding cost effective ways to mass produce graphene. While the original micromechanical cleavage technique [3] (aka Scotch tape) isolated the first single layer graphene flakes, the approach is labor intensive and there is little control on the size and shape of the flakes and their position on a wafer. Other possible routes for the development of graphene have been demonstrated, including growth on SiC [8], Cu [9], Ni [10], and other surfaces.

Oxidized graphene sheets, also known as graphene oxide, may help solve critical issues related to both the mass production of graphene and development of graphene devices. For example, sonication of graphite oxide in water leads to a stable colloidal suspension of graphene oxide platelets that can be further chemically reduced to graphene sheets. Graphene oxide also possesses a band gap and has the potential to serve as a key component in graphene-based electronics such as transistors and Schottky diodes. By selectively oxidizing portions of a graphene sheet, it may be possible to isolate conductive regions and develop barrier layers for electronic devices.

In this chapter, we will explore graphene oxide, the disordered cousin of pristine graphene. The level of oxidation and the specific type and locations of carbon-oxygen bonds that occur make graphene oxide chemically more complex than graphene and difficult to characterize accurately. However, it also provides a crucial example of how both the introduction and removal of surface modifications can affect the structural and electronic properties of graphene. It is important to note that this field is moving rapidly and at best, this chapter will serve as a reasonable and slightly blurry snapshot of current progress. It should provide new researchers with guidance on key issues of
interest and highlight mysteries that still remain for a material discovered over 150 years ago.

1.2 Understanding bulk graphite oxide and graphene oxide monolayers

Since its discovery by Brodie in 1855 [1, 2], several structural models have been developed for graphite oxide (GO). In this section, we will provide a brief overview of the structures that have developed over the years, with a particular focus on how proposed structural elements can help enhance our understanding of the two dimensional analog, graphene oxide (G-O). Given the long history of this material, there have been several excellent reviews of the structural models considered for graphite oxide and graphene oxide [11–13].

![Common functional groups found in graphene oxide](image)

**Fig. 1.1.** Common functional groups found in graphene oxide (a) epoxy group (b) hydroxyl group (c) carbonyl group (d) carboxyl group

The initial studies focused on crystalline models with periodic additions of functional groups to the graphene surface. Diagrams for several common functional groups based on oxygen, carbon, and hydrogen are listed in Fig. 1.1 for the benefit of non-chemists. Hofmann and Holst in 1939 proposed a regular array of epoxy groups (C-O-C) on the graphene surface with a C$_2$O molecular weight [14]. Given experimental evidence for the presence of hydrogen in graphite oxide, Ruess developed a crystalline model for graphite oxide that included both epoxy groups as well as hydroxyl (OH) groups [15]. A important aspect of this model is that each graphene layer is distorted by the presence of the functional groups and the carbon atoms interact through sp$^3$ bonds. Since graphite oxide consists of multiple graphene sheets, bonding of oxygen both above and below an individual graphene sheet is to be expected. Based on experimental evidence that water molecules can be trapped
between layers, Nakajima et al. proposed a model that emphasized the interaction of hydroxyl and carbonyl functional groups trapped between distorted graphene sheets [16]. They argued that the experimentally observed changes in the interlayer spacing in graphene oxide with humidity can be directly related to the ratio of hydroxyl to carbonyl groups, ranging from a completely dehydrated structure, C₈O₂, to a structure dominated by hydroxyl groups, C₈(OH)₄. While this model provides a possible range of structures based on water content, it is important to note that it still relies on a crystalline vision of graphite oxide with a periodic arrangement of functional groups. The wide variety of early structure models developed for graphite oxide is a result of two important issues. The first is due to the fact that the degree of oxidation depends on the fabrication technique used. The other is due to a sparsity of experimental data that allows for accurate characterization of the material at the atomic scale. While it was relatively easy to resolve the average interlayer spacing between graphene oxide layers using x-rays, it has been difficult to resolve whether the sheets are distorted and which specific functional groups are present.

Fig. 1.2. Graphene oxide is typically characterized by an disordered arrangement of oxygen functional groups. This high resolution UHV STM image of oxidized graphene reveals a rare rectangular lattice with a=2.73 Å and b=4.06 Å. The inset shows a proposed graphene oxide crystal structure based on a rectangular lattice of epoxy groups. Adapted from Ref. [17] with permission from Elsevier, copyright 2008.

Unlike the simple honeycomb structure of graphene, the term graphene oxide is best viewed as a concept representing a broad range of disordered oxidized graphene structures where the ratio of functional groups (epoxy, hydroxyl, and carboxyl groups) depends strongly on both the parent material
Graphene Oxide and the processing approach used. Compton and Nguyen recently highlighted this aspect by noting that the carbon to oxygen ratio (C:O) measured in graphite oxide samples ranged from 1.3 to 2.25 depending on the approach used and oxidation time [13]. Lerf et al. were the first group to strongly advocate a structural model based on a nearly amorphous material with a random distribution of regions with unoxidized benzene rings and regions functionalized by epoxy and hydroxyl groups [11]. They also found NMR evidence that the epoxy and hydroxyl groups were usually located fairly close to each other on the graphene sheet. In addition to the presence of both epoxy and hydroxyl groups, they also noted evidence that water molecules could become trapped on the graphite oxide surface. Other groups have also noted that due to its hydrophilic nature, graphite oxide absorbs water under ambient conditions and this may also make characterization difficult. Although there has been one report of graphene oxide with a periodic arrangements of oxygen atoms on portions of the surface [17] (Fig. 1.2), most modern models and experimental measurements of graphene oxide indicate a random distribution of functional groups similar to Lerf et al.’s structure (Fig. 1.3). It is still unclear to what degree the graphene backbone is distorted by the presence of the oxygen functional groups and also whether functional group bonding occurs on one or both sides of graphene. Szabó et al. argued that the carbon backbone would be corrugated with regions of linked cyclohexane chairs and flat carbon hexagons with double bonds [18]. Several groups have found evidence for carboxyl (-COOH) groups that bond on the edges of the graphene sheets. Based on $^{13}$C NMR analysis, Gao et al. have presented a modified version of the Lerf model for Hummers fabricated graphite oxide which also includes five and six-member-ring lactols along the edge of the graphene sheet [19]. They obtain highly conductive reduced graphene oxide by using a three stage process where graphene oxide is first treated with NaBH$_4$ to remove most of the epoxy and hydroxyl groups and break down lactol rings, followed by concentrated sulfuric acid to remove remaining hydroxyl groups, and finally an annealing to eliminate carbonyl edge groups.

This variety of structures due to processing procedure can be beneficial for device applications, because it may provide a way to adjust the band gap of graphene oxide for specific device applications. To help understand the electronic and structure properties of graphene oxide, it is important to consider the key oxygen functional groups that form during the oxidation process and how they interact. A careful study of the energetics of oxygen on a graphene surface should also provide us with knowledge on how to potentially tailor the formation of graphene oxide for specific applications.

### 1.3 Fabrication of Graphite Oxide and Graphene Oxide

Several different approaches exist for fabricating graphite oxide and its two-dimensional analog, graphene oxide. In this section, we will discuss three tra-
ditional approaches used to fabricate graphite oxide and we will also address some recent techniques for the production of graphene oxide. It is important to stress that the exact chemical composition of graphite oxide is process dependent and that the different approaches outlined below can lead to different C:O ratios as well as the presence of different functional groups. Chemical and thermal techniques for producing reduced graphite and graphene from graphite oxide will also be discussed.

### 1.3.1 Traditional Approaches to Fabricate Graphite Oxide

The first production of graphite oxide was done by Benjamin C. Brodie in 1855 who added potassium chlorate (KClO$_3$) to a thick suspension of graphite in fuming nitric acid, HNO$_3$ [1, 2]. He found that the modified graphite crystals consisted of carbon, oxygen, and hydrogen and that the degree of oxidation could be increased by additional treatments of potassium chlorate to the solution, with a final molecular formula of $C_{2.19}H_{0.80}O_{1.00}$. Brodie also noted that graphite oxide was dispersible in water, one of the appealing aspects of this material for industrial applications. Later, Staudenmaier improved Brodie’s technique by adding sulfuric acid to boost the acidity of the mixture as well as adding potassium chlorate at intervals during the reaction [12, 20]. However, this process was time consuming (taking roughly a week) and in early chemical labs, it also presented hazards due to the formation of toxic ClO$_2$ gas.
which can combust in air. In the 1950s, Hummers developed an alternative process for graphite oxide production that could be done in roughly two hours and at lower temperatures [21, 22]. In this approach, a mixture of potassium permanganate (KMnO\textsubscript{4}), sodium nitride (NaNO\textsubscript{3}), and sulfuric acid (H\textsubscript{2}SO\textsubscript{4}) is used to oxidize graphite. Today, Hummers approach with minor modifications is widely used in the field to produce graphite oxide [23, 24]. Excess permanganate ions from the Hummers process can act as contaminants and it is important to remove these with a H\textsubscript{2}O\textsubscript{2} water solution [13, 25]. There is also some evidence that graphite oxide produced using the Hummers approach contains sulfur impurities due to the use of sulfuric acid [26]. Other groups have advocated the use of the Brodie technique, arguing that graphite oxide produced using either Hummers or Staudenheimer can have a high degree of contaminants and can be susceptible to degradation [27, 28].

A recently published paper [29] by Marcano et al. describes an alternative approach to fabricating graphene oxide that increases the amount of potassium permanganate used and excludes the use of sodium nitride. They find that performing the reaction in a 9:1 mixture of H\textsubscript{2}SO\textsubscript{4}/H\textsubscript{3}PO\textsubscript{4} improves overall oxidation, but that the subsequent chemically reduced graphene films have similar electronic properties to sheets generated by other techniques. A key advantage of this new approach is that toxic gases are not produced during the chemical reactions. Luo et al. found that pre-exfoliation of graphite via microwave heating helped to remove intercalated species and improved oxygen absorption in subsequent Hummers processing [30]. This technique was able to generate large graphene oxide flakes (≤ 2000 \(\mu\)m\textsuperscript{2}) with a 90% yield, although the large flake size could also be due to the fact that they do not apply sonication to the samples.

The final molecular composition of graphite oxide depends strongly on the initial graphite sample (i.e. whether the sample has impurities or defects), the oxidizing process used, reaction time, and even humidity. The C:O ratio in graphite oxide can vary from 1.3 (Modified Hummer technique) to 2.28 (Brodie technique) and the intersheet spacing has also been found to range from 5.95 to 8.3 Å. The recent review by Compton and Nguyen [13] provides an excellent table summarizing the oxidants, reaction time, and chemical compositions of graphite oxide formed using the different techniques.

1.3.2 New Fabrication Techniques for Graphite Oxide and Graphene Oxide

The possibility of using graphite oxide as an efficient approach for developing graphene sheets has led to renewed interest in graphite oxide fabrication techniques and approaches to isolate single graphene oxide sheets. Graphite oxide exfoliates in a sonicated water solution into graphene oxide platelets which can then be deposited on surfaces [31]. The formation of thin graphite oxide
sheets in solution was first noted in the original work by Brodie [2] and much later the presence of atomic layers of graphene oxide in solution was confirmed by Boehm et al. in 1962 [32]. These deposited thin films of graphene oxide are composed of stacked and overlapping graphene oxide platelets and it is important to keep this structural model in mind when graphene oxide and reduced graphene oxide thin films are discussed later in the text.

Graphene oxide sheets are generally viewed as being hydrophilic due to the presence of edge carboxyl (-COOH) groups that can ionize [11], making the sheets easy to disperse in water. However, recent research indicates that graphene oxide sheets may actually be amphiphilic with hydrophilic edge groups and a hydrophobic surface and could behave as a surfactant [33]. Due to the large molecular weight of the graphene oxide flakes, it can take several hours for these flakes to equilibrate at the air-water interface. However, this process can be sped up through the use of carbonated water. As CO2 bubbles rise up through the water, amphiphilic graphene oxide platelets become trapped at the water-gas bubble interface and are carried to the water surface via flotation.

The growth of single graphene sheets on several different substrates in recent years has been demonstrated and these films can also be subsequently oxidized [34]. Carbon nanotubes can also be unzipped using potassium permanganate to create graphene oxide nanoribbons [35,36].

**Fabricating reduced graphene oxide**

The ability to fabricate single sheets of graphene oxide via chemical means in solution provides an important base material for the production of reduced or chemically derived graphene (rG-O). With chemical reduction techniques and thermal annealing, it is not possible to completely eradicate oxygen functional groups or structural defects, so reduced graphene has a lower mobility than graphene produced via direct growth techniques or mechanical exfoliation. However, the mobility of these reduced graphene is still comparable to that of doped conductive polymers [37] and could provide a cheap approach for fabricating graphene based electronics.

There are currently several different approaches available to produce reduced graphene oxide. Schniepp et al. showed that rapid heating (> 2000° C/min) of graphite oxide would lead to the release of CO2 and split the remaining material into individual graphene sheets [38]. However, this technique required complete oxidation of graphite to be successful. Stankovich et al. developed a simple approach using hydrazine hydrate to reduce a colloidal suspension of graphene oxide sheets and form reduced graphene oxide sheets [39]. Since graphene oxide is negatively charged in solution, it can also be selectively deposited on predefined positively charged regions on a silicon surface [40]. It has also been shown that reduced graphene oxide films can be fabricated using a combination of hydrazine hydrate and a low temperature
Electrochemical reduction of graphene oxide can also occur in a deaerated aqueous 0.1 M potassium nitrate (KNO₃) solution [42]. Decorating graphene oxide with TiO₂ particles provides an interesting photochemical route to reduce graphene oxide. When TiO₂-graphene oxide nanocomposites are suspended in ethanol and illuminated with ultraviolet (UV) radiation for over 15 minutes, the solution changes color from light brown to black [43]. This indicates increased light absorption similar to what would be found in graphene solutions. In this case, UV radiation leads to charge separation in the TiO₂ particles and the free electrons can reduce epoxy and carboxylate functional groups on graphene oxide. The presence of the TiO₂ particles also insures that the reduced graphene sheets do not agglomerate in solution. Recently, Cote et al. showed that the Xenon flash lamp from a common digital camera could be used to flash irradiate graphite oxide in air and generate patterned regions of reduced graphite oxide [44]. For high power flashes, they also found that rapid degassing and air expansion can lead to complete ablation of the exposed regions and provide a chemical free etching technique.

In 2010, Wei et al. demonstrated that a heated atomic force microscope (AFM) tip (estimated temperature of 1060 °C) can pattern conductive regions of reduced graphene oxide with widths as small as 12 nm (Fig. 1.4) on a graphene oxide film through local annealing [37]. This opens an interesting route for patterning nanoscale graphene devices in graphene oxide sheets. In addition, a recent study has shown the reduction of graphene oxide can occur via bacterial respiration using microbes (genus Shewanella) that are heterotrophic, facultative anaerobes [45]. This could provide an unique chemical free and green route to reduced graphene oxide.

**Fig. 1.4.** (a) Room-temperature AFM current image of a zigzag-shaped nanoribbon fabricated by thermochemical nanolithography on epitaxial graphene oxide. (b) Corresponding topography image take simultaneously with (a). (c) Averaged profiles of current and height of the cross sections that are indicated as dashed lines in (a) and (b). From Ref [37]. Reprinted with permission from AAAS.
Chemically derived graphene has a much lower electrical conductivity than pristine graphene which indicates that defects or scattered functional groups remain after the reduction process. The exact mechanisms for the removal of oxygen functional groups by chemical means \( \text{i.e.} \) hydrazine \( (\text{N}_2\text{H}_4) \) or by annealing has been unclear. Recently, Gao, Jang, and Nagase examined different reaction pathways for hydrazine and thermal reduction of graphene oxide using density functional theory \([46]\). They found that hydrazine is effective at removing epoxy groups in aromatic regions of graphene oxide via three different mechanisms, but converts edge epoxide groups to stable hydrazino alcohols that are difficult to remove. The presence of stable hydrazino alcohols on the edges of chemically reduced graphene sheets is supported by several experimental studies that find a significant amount of nitrogen in hydrazine reduced graphene oxides \([39, 47, 48]\). Gao, Jang, and Nagase find that hydrazine has no effect on hydroxyl, carboxyl, and carbonyl groups which must be removed using a high temperature thermal treatment. Reaction energetics indicate that the efficiency of hydrazine removal of epoxy groups \textit{decreases} as temperature increases. Therefore, they suggest a two stage reduction process with a low temperature chemical reduction for epoxy groups followed by a \( >700^\circ\text{C} \) thermal annealing treatment. They propose the use of \( \text{PPh}_3 \) as the reducing agent catalyzed by \( \text{MeReO}_3 \) in \( 55^\circ\text{C} \) toluene. Recent studies have shown that catalyzed \( \text{PPh}_3 \) can effectively remove epoxides both on graphite surfaces and edges \([49, 50]\), which could make it a superior graphene oxide reducing agent to hydrazine.

Molecular dynamics studies also help to provide insight into the local bonding structure in thermally reduced graphene oxide \([51, 52]\). Bagri et al. examined a graphene oxide sheet with an initial random configuration of epoxy and hydroxyl groups on the carbon backbone \([51]\). Using molecular dynamics simulations with the ReaxFF potential \([53]\), the model graphene oxide sheet was annealed at 1500 K. They found that the reduced graphene oxide films were characterized by a large number of stable holes which form when C-C bonds break in the basal plane. These holes are decorated with a carbonyl and hydroxyl group or else two carbonyl groups. First principle simulations indicate that these holes form to relieve the stress in the carbon backbone induced by epoxy groups. The analysis of the molecular dynamics simulations also appears to be supported by additional transmission infrared and XPS spectra of reduced graphene oxide \([52]\). Based on these molecular dynamics simulations, they suggest that the primary culprit for poor reduced graphene oxide film quality (presence of holes, carbonyl groups) is due to the epoxy functional groups that strain the carbon backbone and promote C-C bond breaking and emission of CO and CO\(_2\) from the film. To help ameliorate this issue, Bagri et al. propose a subsequent reheating of reduced graphene oxide in a hydrogen atmosphere to help heal the graphene lattice \([52]\).
1.4 Characterization Approaches

1.4.1 Optical Microscopy

For general assessment of graphene and graphene oxide sheets for possible device fabrication, optical microscopy remains the leading high throughput and low-cost imaging approach in the field. Although graphene absorbs a relatively high percentage of visible light (2.3 %) for a single atomic layer [54], it is difficult to obtain high contrast images of graphene based on transmitted light. Reflective illumination techniques can provide high-contrast optical images of graphene and graphene oxide. The addition of a single atomic layer (like graphene) to a dielectric layer grown on a reflective substrate alters the optical path of reflected light enough to change the reflected color [55]. This allows researchers to rapidly scan through large sections of deposited graphene sheets and measure graphene flake sizes, layer thickness, and wrinkles. In their seminal work on graphene [3], Novoselov et al. used this technique to resolve graphene layers deposited on oxidized silicon. Later works have focused on optimizing the dielectric material and layer thickness to provide high-contrast optical imaging for graphene oxide [56] and graphene [57]. However, it should be noted that reflective illumination requires that graphene is deposited on a dielectric coated silicon wafer with an optimized oxide thickness. Recently a group has developed a new technique for large scale imaging of graphene and graphene oxide that is based on fluorescence quenching [58]. Graphene based materials have a strong quenching effect on fluorescence dyes. Upon excitation, graphene platelets, on a surface that has been coated with fluorescence dyes, appear as dark shapes in a bright background. Since this approach does not rely on interference effects, it can be used to characterize graphene and graphene oxide deposited on a range of substrates, including plastics and glass.

1.4.2 Scanning Transmission Electron Microscopy

Many graphene oxide research articles include conventional phase-contrast TEM images of the sheets. While these relatively low-magnification TEM images are quite useful to visualize the sheets, they contain very little information about the internal atomic structure of the sheets. For structural characterization, diffraction patterns are often obtained from the individual sheets [59,60]. These diffraction patterns are the result of electron beam scattering from wide ≥ 100 nm areas of the specimen and can only describe the underlying long-range periodic arrangement of the atoms. They cannot be used to identify unique defects or short-range structural alterations in the sheets. However, when the operational conditions of the electron microscope are optimized to minimize possible electron beam induced damage of the sheets [61], recorded atomic-resolution images can reveal many interesting structural features in the sheets. The recent report by Gomez-Navarro et al. [62] is a good example
of using high-resolution phase-contrast TEM imaging to detect and characterize defects in a single layer reduced graphene oxide sheet. As can be seen in Fig. 1.5, the atomic-resolution TEM image clearly reveals that the sheets are composed of intact 3 and 6 nm graphene islands along with various topological defects and deformations. Using TEM images, defects such as carbon pentagons, hexagons, and heptagons, dislocation dipoles, defect clusters, distortions in the hexagonal lattice can be identified.

**Fig. 1.5.** TEM image of a single layer reduced-graphene oxide membrane. (a) Original image and (b) with color added to highlight the different features. The defect free crystalline graphene area is displayed in the original light-gray color. Contaminated regions are shaded in dark gray. Blue regions are the disordered single-layer carbon networks, or extended topological defects. Red areas highlight individual ad-atoms or substitutions. Green areas indicate isolated topological defects, that is, single bond rotations or dislocation cores. Holes and their edge reconstructions are colored in yellow. Scale bar 1 nm. Reprinted with permission from [62]. Copyright 2010 American Chemical Society.

Scanning transmission electron microscopy (STEM) is often the preferred approach for quantitative analysis of the local atomic structure and composition of graphene oxide. STEM with a high-brightness field emission electron source, scanning with a focused electron probe, and the annular dark field (ADF) detector is an alternative approach for atomic-resolution imaging to conventional TEM with additional analytical capabilities [63]. The success of the STEM for quantitative imaging at high-resolution is governed by the ability to record images of the specimens by collecting elastically scattered probe electrons using a high-angle ADF detector. This allows visualization of specimens at resolutions smaller than 1 Å with simplicity of interpretation: the heavier the atoms, the stronger the scattering and, as a result, the brighter the signal [64–66]. The simplicity of the method and the relatively weak dependence of ADF imaging on microscope focusing conditions and specimen thickness allows very little room for error. For example, an ADF-STEM approach can image individual dopant atoms inside a silicon crystal [67] and reveal anomalies in the local thermal vibration of atoms in a quasicrystal [68].
Several ADF-STEM studies of graphene and graphene oxide sheets have been reported [69–71]. An ADF image of several layers of graphene oxide suspended over a hole is shown in Fig. 1.6(a). The mono, bi-, and trilayered films can be clearly imaged, even though the signal from the single layer appears to be weak and barely distinguishable from the hole. A high-magnification ADF image taken from the single sheet with O:C = 1:5, shown in Fig. 1.6(b), reveals not only the sheet but also the variation of intensities within the image, indicating that the oxidation of the graphene is uniformly random throughout the sheet.

![Fig. 1.6.](image)

For a better realization of the possibilities with ADF-STEM imaging in characterization of the graphene oxide films, several ADF-STEM images were simulated and two of them are presented in Fig. 1.6(b,c). These ADF images were simulated using the *Multislice* method [72]. The results suggest that the ADF detector can be used to not only directly image single oxygen atoms on the graphene substrate, but also identify the actual oxygen bonding sites on the carbon honeycomb structure.

### 1.4.3 Electron Energy Loss Spectroscopy

STEM combined with electron energy loss spectroscopy (EELS) is a very effective method for measuring electronic and optical properties of nanoscale materials [73]. When core-level electronic transitions are recorded with EELS, it is possible to carry out an analysis of the local chemistry and electronic structure. The Fermi golden rule describes the physics of these transitions and shows the element- and site-specific nature of these localized core-level transitions. A simple and intimate connection between the local density of unoccupied electronic states and the core-level excitations allows EELS to
directly measure both the energy distribution and density of states for levels above the Fermi energy \[74,75\].

Mkhoyan et al. \[71\] reported core-level EELS measurements from a single graphene oxide sheet. Spectra of C and O K-edges (Fig. 1.7), which are the result of 1s to 2p electronic transitions in carbon and oxygen atoms, represent the respective 2p partial density of states of the conduction band of graphene oxide. As can be seen from Fig. 1.7 (a) the fine structure of the C K-edge in graphene oxide shows considerable differences in fine structure relative to those in graphite and amorphous carbon (a-C). Removal of the STEM probe function from the measured C K-edge enhances the fine structure as shown in Fig. 1.7(c). The analysis of the positions of identifiable peaks in a C K-edge in all three materials suggests that both sp\(^2\) and sp\(^3\) bonds are present in the graphene oxide. Additionally, for quantitative analysis, the EELS spectrum of the C K-edge can be fitted to a linear superposition of two spectra, C K-edge from graphite and amorphous carbon (a-C). For a O:C ratio of 1:5, as much as 40% of the carbon bonds are transformed into sp\(^3\) bonds. The fine structure of the O K-edge, which lacks distinct features, presented in Fig. 1.7(b), indicates the absence of periodicity for the oxygen atoms in the film and shows strong similarities with the O K-edge of amorphous SiO\(_2\).

![Fig. 1.7. Core-loss EELS spectra of (a) C K-edge and (b) O K-edge from the graphene oxide film. The spectrum of C K-edge is presented in comparison with C K-edges measured in graphite and a-C. The peaks of the fine structure are labeled A to E. The inset shows the section of the spectrum from graphene oxide for better visibility of the positions of the peaks B (or \(\sigma^*\)) and C. The O K-edge is presented in comparison with O K-edge in a-SiO\(_2\). (c) The spectrum of the C K-edge in graphene oxide film and its best fit after removal of STEM probe function. Reprinted with permission from \[71\]. Copyright 2009 American Chemical Society.

The low loss region of EELS, on the other hand, measures optical properties of the specimens by recording electronic transitions between critical points of conduction and valence bands as well as characteristic plasmon ex-
citations, which leads to the real and imaginary parts of dielectric function of the material [73]. The low-loss EELS spectrum was recorded from a single graphene oxide sheet [71]. The low-energy plasma excitations of the π* electrons in graphene oxide occurs at 5 eV, similar to that in a-C. While the peaks of bulk plasma-loss (combination of π* and σ* electronic excitations) for graphite and a-C occur are at 27 and 24 eV, respectively, in graphene oxide films, it appears to be at 19 eV. Since the thickness of the film is only ~1 nm thick, a full quantum mechanical description is needed to understand this 19 eV plasmon peak. A recent study by Eberlein et al. that combined EELS measurements with first principle calculations indicates that the plasmon modes of pure graphene are expected to have a significant red-shift from those found in graphite. They measured the main π* + σ* plasma peak at 14.6 eV and a π* peak at 4.7 eV [69,70].

1.4.4 Atomic Force Microscopy

The atomic force microscope (AFM) was invented and introduced by Binning, Quate and Gerber in the mid-1980s [76]. It was based on the scanning tunneling microscope (STM) and took advantage of the existence of strong interatomic forces between atoms at the specimen surface and the scanning tip. For a good overview of STM and its use in characterizing graphene, please see Chapter 3 in this book. AFMs, which can operate in contact and non-contact mode, are extensively used in surface sciences and can even determine the structure of solid surfaces with atomic-resolution. A benchmark atomic-resolution AFM image of the Si(111)-(7x7) surface was recorded by Giessible [77] in 1995. In-depth discussion on the principals of operation and achievements of atomic-resolution AFM can be found in recent book by Morita et al. [78] and in review by Giessible [79].

While atomic-resolution imaging of pristine solid surfaces using AFM can be challenging experimentally, measuring the atomic steps present on surfaces is relatively easy. This ability of AFM to determine z-heights of specimens with atomic precision makes it exceptionally suitable for measuring the thickness of graphene oxide sheets. Two examples of AFM images of graphene oxide sheets are presented in Fig. 1.8 [59]. The thickness of single or multiple sheets can be obtained either by taking a simple line-scan going across the sheets and substrate as shown in Fig. 1.8 (a) or by obtaining the histogram of the area of interest in the image as shown in Fig. 1.8 (b,c) [71].

The typical thickness of a single graphene oxide sheet is within the range of 1 to 1.6 nm and it is thicker than a pristine graphene sheet, which is only 0.34 nm [39,71,80]. This is most likely due to the presence of different functional groups at either surfaces of the graphene oxide as well as some adsorbed molecules. It is also expected that some water molecules might be trapped between the sheet and substrate or between the sheets, since these functional groups make graphene oxide strongly hydrophilic [11,80,81]. When a large scale AFM scan is performed with many graphene oxide sheets, statistical
Fig. 1.8. (a) AFM image of graphene oxide sheets deposited onto a mica substrate obtained using the non-contact-mode from an aqueous dispersion (inset) with superimposed cross-section measurements taken along the red line indicating a sheet thickness of ∼1 nm. [59]; (b) AFM image of the graphene oxide sheets where mono-, bi-, and trilayers can be identified; (c) histogram of the AFM-depth intensities obtained from dotted area of the image (b). The histogram is fitted with a linear combination of four Gaussian functions representing each peak. Reprinted with permission from [71]. Copyright 2009 American Chemical Society.

analysis can be carried out to quantify the size distribution of the sheets [82,83].

1.4.5 X-ray Photoelectron Spectroscopy

When overall compositional analysis of the graphene oxide sheets is needed and atomic-scale structural details are not critical, X-Ray Photoelectron Spectroscopy (XPS) is an excellent alternative technique. Keeping in mind that the results of the XPS reflect the average X-ray response of the specimen, the measured spectra can reveal the presence of elements in the sheets (carbon, oxygen, hydrogen etc.), their relative fractions, and the nature of the bonds [84,85]. However, to carry out compositional and structural analysis of graphene oxide with XPS, several precautions should be taken. For reliable measurement of the XPS spectra from a single sheet of graphene oxide, it is essential to develop a routine that will allow for controllable and systematic deposition of a single sheet of graphene oxide on the substrate. Since single sheets of graphene oxide are ∼1 nm thick, the presence of peaks from substrate elements in the measured XPS spectrum is unavoidable. Additional measurements from substrate-only regions might be needed. To minimize the effects of the substrate, a careful selection of the substrate can be instrumental. For XPS study of graphene oxide sheets, a preferable substrate should not contain elements such as carbon or oxygen or hydrogen. However, additional care must be taken even with those substrates, since most of the practical surfaces exposed to air easily experience oxidation.

Fig. 1.9 shows XPS data recorded from a single layer graphene oxide film deposited on Au coated SiO$_2$/Si substrate, which was later annealed at different temperatures in ultra-high-vacuum (UHV) for oxygen reduction [86]. The
C 1s signal typically consists of five different chemically shifted components: C=C/C-C in aromatic rings (284.6 eV); C-O (286.1 eV); C=O (287.5 eV); C(=O)-(OH) (289.2 eV); and $\pi - \pi^*$ satellite peak (290.6 eV) [86–89]. For quantitative analysis, the spectrum of C 1s can be decomposed into individual components by fitting the entire spectrum to a linear superposition of all components present. This decomposition allows determination of the fractions of each component. Additionally, the fraction of sp$^2$ and sp$^3$ C-C bonds can be estimated by evaluating the intensities of the corresponding components.

![Fig. 1.9](image.png)

The C-O bonds in graphene oxide is thought to come predominantly from epoxy and hydroxyl groups in the basal plane. The XPS measurements of O 1s, which includes typical contributions from C=O (531.2 eV), C-O (533 eV) and C(=O)-(OH) (533 eV) bonds, can be used to estimate the fraction of these groups present on sheets [87, 89]. An example of the O 1s XPS spectra from single layer graphene oxide and reduced graphene oxide is presented in Fig. 1.9(b).

1.4.6 Raman Spectroscopy of Graphene Oxide and Reduced Graphene

Raman spectroscopy can provide important information regarding the bonding configurations of atoms in carbon structures. This technique relies on illuminating a material with a laser and observing how inelastic scattering with lattice vibrations or phonons affects the photon energy. Conjugated carbon
atoms and carbon atoms with double bonds give particularly strong Raman signals. A full discussion of the Raman spectroscopy of graphene can be found in Chapter 2 of this book. In this section, we will briefly highlight those aspects relevant to graphene oxide research.

The Raman spectra of graphite has a dominant peak (G band) at roughly $1580 \text{ cm}^{-1}$ that is due to an $E_{2g}$ optical phonon mode that involves in-plane $sp^2$ bond stretching of the graphite lattice. A much smaller peak known as the D band is located at a lower frequency $1355 \text{ cm}^{-1}$ and is due to a breathing mode of the hexagonal carbon rings. It is Raman inactive in pristine graphite and the observed D band peak can be related to disorder along the edges of the graphite sample. The overtone of the D band, known as 2D, however is Raman active even in pristine graphene and is due to double resonance transitions that generate two phonons with opposite momentums. The 2D peak can be used to determine the number of layer in pristine graphene multilayers [90–92], but it can be difficult to observe in graphene oxide samples.

During oxidation, the intensity of the D band increases significantly, indicating increased disorder and symmetry breaking in the graphene layers. The G band peak becomes broader and also experiences a blue shift to roughly $1593 \text{ cm}^{-1}$. Upon transforming graphite oxide to reduced graphite, the G band peak returns to the original graphite frequency, indicating that the presence of oxygen could be related to the observed blue shift.

Using the Tuinstra-Koenig relation [93], the area ratio of the D and G peaks can be used to determine the size of $sp^2$ clusters in a $sp^2$ and $sp^3$ carbon network. Analysis of Raman spectra indicates that graphene oxide films can possess graphitic domains with sizes ranging from 2.5 to 6 nm. Above a critical defect density (< 2 nm $sp^2$ cluster size), the Tuinstra-Koenig relation fails and can not be used to interpret the Raman spectra. There has also been some difficult in interpreting the D/G ratio during graphene oxide reduction, since contradictory trends have been observed. A recent study [94] has shown that the ratio of 2D/G may provide a better measure of the extent of graphitic $sp^2$ region as demonstrated by a linear dependence of the 2D/G ratio with electron mobility for graphene oxide films (Fig. 1.10).

Using Raman spectra calculated with density functional perturbation theory [95], Kudin et al. found that a modified form of Scholz-Boehm proposed GO structure provided the best spectral match and reasonable agreement with elemental composition [96]. This structure consists of wide ribbons of $sp^2$ bond carbon separated by parallel hydroxyl chains. A small concentration of epoxy groups are also located within the $sp^2$ regions. The wide $sp^2$ ribbons are necessary to produce delocalized $\pi$ electrons and the presence of the random epoxy groups are necessary to block additional Raman spectral peaks in the modified Scholz-Boehm structure that are not observed in experiment. However, despite the good match with the Raman spectra, the graphene oxide structure proposed by Kudin et al has not been observed experimentally, indicating that another explanation for the Raman shift may exist.
Fig. 1.10. Raman spectra for 5 selected transistor devices with various values of effective mobility. The labels M0.4, M1.0, M4.6, M6.9, and M12 represent the devices with mobility 0.4, 1.0, 4.6, 6.9, and 12 cm$^2$/(V s), respectively. (b) Various ratios for the integrated peak area for D, G, 2D, and D+G bands. Reprinted with permission from [94]. Copyright 2009 American Chemical Society.

1.5 Insight from simulations

Nanoscale simulations can provide important insights into the structural, electronic, and chemical properties of graphene oxide. Empirical tight binding calculations coupled with results from detailed density functional approaches can provide important insight into physical and chemical bonding. In recent years, these tools have also been brought to bear on the question of graphene oxide formation, structure, and reduction to graphene.

1.5.1 Using Epoxy Groups to Unzip Graphene

Numerous experimental studies of graphene oxide have indicated the presence of single oxygen atoms bonded to two carbons, otherwise known as epoxy groups (C-O-C). Electronic structure studies have also shown that oxygen atoms situated above a C-C bond provide one of the most stable bonding locations for oxygen on a graphene sheet [71]. The presence of the oxygen atom acts to locally distort the graphene sheet, with the C-C distance of the nearest neighbor C atoms increasing from a sp$^2$ bond length to a bond length much closer to a sp$^3$ configuration.

In many graphite oxide samples, cracks and fault lines are noticeable under inspection using optical and force microscopy techniques [97, 98]. These boundary regions play an important role in the evolution of graphite during oxidation and may be central to the controlled formation of small reduced graphene oxide flakes. As such, a clear picture of the local atomic structure is crucial for understanding the oxidation process.

This issue was first addressed in 2006 by Li et al. [97] who used density functional theory to help resolve the formation of these cracks in small
graphene platelets, C\textsubscript{12}H\textsubscript{24} and C\textsubscript{54}H\textsubscript{12}. They focused in particular on the bonding of individual oxygen atoms (epoxy groups) on a single side of the graphene surface and how these functional groups strain the surface. The distance between the carbon atoms participating in the oxygen bond is transformed from sp\textsuperscript{2} to sp\textsuperscript{3} character and their energetic analysis indicates that epoxy groups prefer to form line structures (grain boundaries) on the graphene surface. It is important to note that the predicted hopping barrier for epoxy groups moving on a graphene surface is fairly large (0.9 eV) and this may prevent the formation of long epoxy chains in some cases. Li et al. argue that this barrier may be lower in solution, but this calculation has not been performed.

A later theoretical study [99] of an epoxy grain boundary noted that while the epoxy functional groups do increase the local C-C bond length, the structure is still stable and the presence of epoxy groups is not sufficient to fully unzip the graphene sheet. They find that the formation of carbonyl (C=O) groups along the chain is necessary to rip the sheets apart. They also examine the possibility of graphene tearing from carbonyl groups at the graphene sheet edge and found this to be energetically unfavorable. It is interesting to note a recent study [98] where graphene nanoribbons are sonochemically cut from chemically derived graphene sheets along fault lines possibly made up of epoxy functional grain boundaries.

The formation of epoxy chains on one side of the graphene sheet may be energetically favorable for the oxidation of graphene sheets resting on a substrate. However, in the case of the oxidation of graphite, the relatively large distance between graphene sheets allows oxygen to bond on either side of a given graphene sheet. In this scenario, other oxygen bonding configurations may be more energetically favorable. In the case where neighboring epoxy group in the chain are on opposite sides of the graphene sheets, the local strain on the carbon atoms is significantly reduced and the carbon bond preserve more of their sp\textsuperscript{2} character. A recent density functional study found that fault lines that include a combination of both epoxy and hydroxyl groups (2O+2OH) are more energetically favorable than an epoxy chain on one side of the graphene sheet [100]. This corresponds well with experimental evidence that indicates epoxy and hydroxyl groups are usually located near each other on the carbon backbone. Whether oxidation can occur on both sides of a graphene sheet rather than a single side could have important consequences on the degree of local strain placed on carbon bonds. A greater portion of sp\textsuperscript{3} bonds should occur in graphene oxide with single sided growth due to epoxy groups. In cases where oxidation occurs on both sides, several atomistic studies show that stress fields can effectively cancel each other out and help maintain the hexagonal carbon network, leading to a smaller number of sp\textsuperscript{3} bonds [100–102].

While the original work of Li et al. focused on the development of epoxy chainlets, it would be helpful to examine the energetics of long epoxy chain growth on large graphene sheets to insure that edge effects do not play a role. A recent paper [103] examined the distribution of
functional groups on a graphene surface using a combination of density functional theory and Monte Carlo techniques. They found that an epoxy chain with four atoms would be stable, but they did not find evidence that chain growth beyond this length would be encouraged.

1.5.2 Graphene oxide electronic structure

Due to the random distribution of epoxy and hydroxyl groups on the surface of graphene oxide, it is difficult to discuss the electronic structure in terms of a crystalline band structure model. A number of groups have used density functional theory to examine the energetics of possible crystalline configurations of graphene oxide, but these ordered structures appear to be difficult to fabricate with current chemical techniques, given that only one paper [17] reports an ordered graphene oxide region. Several experimental studies have shown that graphene oxide can be viewed in terms of fairly large insulating \( \text{sp}^3 \) regions surrounding small \( \text{sp}^2 \) islands [71]. In such a scenario, we would expect electrical transport to be primarily based on hopping between localized states in a percolation framework.

First principle calculations can provide insight into how functional groups affect the local electronic structure in graphene oxide. As an example, we can examine the local density of states near a single epoxy group on a graphene sheet (Fig. 1.11). The relaxed structure for the epoxy group is determined using a density functional calculation as outlined in Mkhoyan et al. [71]. The density of states for pristine graphene is shown in comparison with both the local density of states of a carbon atom in the epoxy group and one far away from it. For the carbon bond participating in the epoxy group, the \( \pi^* \) peak is no longer present and the local density of states near the Fermi energy is significantly reduced. The \( \pi^* \) peak is stable for a carbon atom located far from the stress field created by the epoxy bond.

Fully oxidized graphene has a light brownish color and is fully insulating with a direct optical band gap of 2.4 eV [104]. Optical studies indicate that the band gap of graphene oxide can be increased (decreased) through oxidation (reduction) [104, 105]. Jeong et al. found that the graphene oxide optical band gap could be adjusted from 1.7 eV (semiconducting) to 2.4 eV (insulating) in strong correlation to the oxygen to carbon ratio. The graphene oxide in this case was prepared using a simplified Brodie technique [28]. Blue photoluminescence from graphene oxide has also been found to depend on the degree of chemical reduction [105, 106].

For graphene structures with ordered or crystalline oxygen functional groups, density functional calculations indicates that the band gap also increases with the oxygen carbon ratio [102, 107]. Yan, Xian, and Chou considered graphene oxide as an effective alloy consisting of three components, \( \text{sp}^2 \) C, epoxide groups (\( \text{C}_2\text{O} \)), and 1,2-hydroxyl pairs (\( \text{C}_2\text{(OH)}_2 \)), with relative proportion based on the degree of oxidation [100]. Based on density functional
1.5.3 Electron mobility and transport

Since a great deal of research has been focused on mass production of graphene sheets from graphene oxide, the electron mobility of the reduced graphene oxide sheets has been an area of considerable interest and investigations. As we have seen throughout this chapter, the parent graphene oxide material can be thought of as a graphite backbone with a random distribution of oxygen functional groups (primarily epoxy and hydroxyl groups) on the surface. The presence of the functional groups leads to local strains and distortions of the honeycomb lattice and the subsequent transformation of sp$^2$ bonds into sp$^3$ bonds. In this sense, graphene oxide can be thought of as a material consisting of small sp$^2$ or conductive graphene islands surrounded by a sea of disordered, insulating sp$^3$ regions. By reducing a graphene oxide sample, a large number of sp$^2$ bonds can hopefully be restored to provide a conductive path across the film.

Discussions about transport in graphene oxide [108, 109] have focused on a variable range hopping regimes where electrons hop between localized sp$^2$ states. In this model, the conductivity can be expressed as:

Fig. 1.11. *Ab-initio* calculated electronic structure of a graphene sheet with a single oxygen atom (epoxy group) bonded to two adjacent carbon atoms. (b) Carbon 2p partial density of states for graphene and for C atom of graphene bonded to O and one that is far away from O. Reprinted with permission from [71]. Copyright 2009 American Chemical Society.

calculations of ordered structures in the ternary diagram, they also found that the band gap increased with the oxygen to carbon ratio.
\[ \sigma = \sigma_0 \exp \left( \frac{-B}{T^{1/3}} \right) \]  

(1.1)

where \( T \) is the temperature and the hopping parameter \( B \) can be related to the wavefunction decay constant and the density of states at the Fermi energy. For graphene oxide samples that has not undergone a full reduction process, the experimental conductivity does show a linear trend when plotted against \( T^{-1/3} \), supporting the variable hopping model [108,109]. Through analysis of different graphene oxide samples at various degrees of reduction, Eda et al. found that the change in the \( B \) parameter could be related to an increased number of localized states near the Fermi energy, but that the decay parameter or localization length for electrons still remained roughly constant [109,110]. This indicates that while reduction may result in additional \( sp^2 \) islands, boosting the number of localized states, they are still, for the most part, not connected and this prevents the electrons from becoming itinerant. A transition from the variable hopping regime to a semimetal reduced graphene oxide with band-like transport was observed when the samples were well reduced. This is most likely due the formation of a percolation regime with greater connectivity between \( sp^2 \) islands, electron delocalization, and the formation of efficient electrical paths through the sample. Mattevi et al. found that this transition to a percolation regime occurred at a \( sp^2 \) fraction of \( \approx 0.6 \) [86].

Since the transport mechanism depends strongly on the degree of oxidation and oxidation procedure, it is not surprising that the measured mobilities vary widely between different groups. Eda, Fanchini, and Chhowalla grew graphene oxide using a modified Hummers approach and then used a combined hydrazine and thermal annealing method to reduce their samples [41]. They found this technique worked better than separate chemical or thermal annealing. Hole mobilities of the flakes ranged from 2-200 cm\(^2\)/Vs and the mobility for a thin film transistor with a long channel length (400 \( \mu \)m) was much smaller 1 cm\(^2\)/Vs and this reduction could be due to scattering at junctions between flakes [41].

Gomez-Navarro et al. used Hummers graphene oxide that was chemically reduced with hydrazine and found conductivity ranges from 0.05 - 2 S/cm and field effect mobilities of 2-200 cm\(^2\)/Vs at room temperature [111]. Several additional groups [112,113] have fabricated graphene FETS with hole mobilities ranging from 0.25 cm\(^2\)/Vs to 4 cm\(^2\)/Vs and max electron mobilities of 1 cm\(^2\)/Vs. Recently Shin et al. found that reducing graphene oxide with sodium borohydride (NaBH\(_4\)) leads to a much smaller sheet resistance than graphene oxide reduced using hydrazine (N\(_2\)H\(_4\)) [114]. Wang et al. observed that electron mobility was higher than hole mobility in contrast to other experimental studies. They found a maximum transistor mobility of 10 cm\(^2\)/Vs [115].
1.6 Applications for Graphene Oxide

1.6.1 Graphene Oxide Electronics

Optical studies of graphene oxide have shown that the band gap of the material can be adjusted by the relative amount of oxidation [105]. This also leads to a measurable drop in the transparency of graphene oxide films during reduction. This ability to control the electronic properties of G-O makes it an appealing component for graphene based electronics. In 2008, Wu et al. examined the transport properties of graphene/graphene oxide junctions using both chemically derived graphene oxide flakes and graphene oxide formed from epitaxial graphene [34]. Transport measurements indicate the presence of Schottky barriers at the G/G-O interfaces with a height of 0.7 eV. The barrier height reduces with annealing (0.5 eV), which indicates that the degree of oxidation directly affects the band gap of graphene oxide.

Transparent conducting films based on graphene oxide were first demonstrated in 2007 [116]. The graphene oxide sheets were mixed with silica in solution and could be easily spin coated onto glass. Through careful processing, nanometer graphene oxide films can be reduced sufficiently to have both high conductivity and high optical transparency. Films with sheet resistances of $\approx 1 \ \text{k}\Omega/\text{sq}$ and 90% transparency have been achieved with high temperature pyrolysis (1000 $^\circ\text{C}$). Reduced graphene oxide electrodes could provide a cheap alternative to indium tin oxide (ITO) electrodes. Graphene also has a very similar work function to that of ITO, which should allow for easy integration into existing photovoltaic and LED device designs. However, the development of fabrication techniques that do not rely on high temperature pyrolysis will be essential for these devices to be competitive [110].

Typically for electronic applications of graphene oxide, the in-plane electrical conductivity is of primary importance. A recent work by Li et al., however, presents an interesting application of graphene oxide for solar cells where the conductivity perpendicular to the plane is the key metric for device performance [117]. In composite organic photovoltaics, the active region consists of acceptor nanostructures embedded in a donor polymer matrix which provides a large acceptor/donor interface surface area for effective charge separation. The efficiency of these devices can be limited by charge recombination when the anode and cathode contact both donor and acceptor regions in the photovoltaic. To block electrons and prevent charge recombination, thin p-doped layers or hole transport layers are often deposited on the anode [118, 119]. However the need to vacuum deposit inorganic hole transport layers makes fabrication much more costly and removes any advantage in comparison to traditional solar cell technology. Hole transport layers that can be deposited in solution are known (i.e. PEDOT:PSS), but the deposition process required can degrade device performance. Li et al. found that a 2 nm graphene oxide layer can serve as an effective hole transport layer with an estimated band gap of 3.6 eV. They view graphene oxide as a graphene sheet covered primarily by wide band semiconducting regions due to $\text{sp}^3$ bonds with scattered
The large band gap regions effectively blocks electron transport into the anode and the efficiency may be further improved by reducing the size of the sp² regions.

A group has recently demonstrated that graphene oxide can be used an effective charge trapping layer dielectric in memory storage devices where the threshold voltage is dictated by the charge trapped in the graphene oxide sheet [120]. These devices demonstrate a large memory window (7.5 V) which is essential for nonvolatile memory applications. The memory window is also significantly larger than previous devices based on carbon nanotubes [121] (0.4 V) and it can be adjusted over a range of (1.4 V to 7.5 V) with chemical reduction. Due to the fact that graphene oxide can be processed in solution, it may provide an important memory component for flexible organic electronics.

The ability to store charges is also extremely important for capacitor applications. Electrochemical double layer capacitors (EDLCs) store charge by reversibly absorbing electrolyte ions on electrodes. In order to store a significant amount of charge, a large surface area is crucial. Typical high surface area electrode materials for EDLCs are based on a combination of activated carbon and carbon black filler and provide capacitances ranging from 120 F/g (organic electrolyte) to 300 F/g (aqueous electrolyte) [122]. Reduced graphene oxide films have a large surface area (400-700 m²/g) and also exhibit very encouraging capacitances with 120 F/g (organic) [123] and 190 F/g (aqueous) [124]. Work is currently underway to enhance the surface area of graphene oxide layers through the use of spacers to prevent agglomeration. A more detailed discussion of the use of graphene oxide materials in capacitors can be found in Ref. [125].

### 1.6.2 Sensors

While the functional groups in graphene oxide are often used to adjust the electronic structure of the graphene sheet [105], they also offer important functional sites for biological and chemical applications. A research group has recently demonstrated a glucose biosensor based on a graphene oxide electrode [126]. The graphene oxide is functionalized by covalently bonding glucose oxidase amines to carboxyl acid groups on the surface. The functional modified graphene oxide sensor demonstrates a reproducible linear response over a wide range of glucose concentrations and initial studies indicate it could be biocompatible with human cells. Another group has also found that reduced graphene oxide sheets can serve as effective chemical sensors with parts per billion detection levels for chemical warfare agents and explosives [127].

### 1.6.3 Carbon-based magnetism

The development of nanoscale magnetic structures for memory applications and possibly spin based electronics such as magnetic tunnel junctions has been one of the main drivers for top down nanoscale fabrication. Magnetic
materials used in industry rely on elements with \( d \) or \( f \) orbital electrons. The possibility of developing magnetic materials based on light elements with no \( d \) orbitals, such as carbon nanotubes and graphene, has been an active and controversial field [128]. Ferromagnetism in high pressure rhombohedral \( \text{C}_{60} \) was reported with a \( T_C \) of 500K in 2001 [129], but the work was later retracted when the results could be explained with the measured amount of magnetic (Fe) impurities in the sample [130]. However, more recent experiments using proton irradiated highly orientated pyrolytic graphite (HOPG) [131] and pristine graphite [132] have shown evidence of room temperature ferromagnetism. In addition, density functional calculations of graphene nanoribbons provide evidence of localized magnetic moments on surface or edge states. The review by Yazyev [128] is an excellent source for additional information of the numerous experimental and theoretical studies of magnetism in carbon nanostructures that have come out recently.

In this work, we will only highlight recent works in the past year that have considered magnetism in graphene oxide structures. Using magnetic susceptibility measurements, Lee et al. found that magnetism in graphite oxide fabricated using the Staudenmaier approach could occur due to the localization of graphite free electrons [133]. Based on Fourier transform infrared spectra, they found that epoxy groups were the primary functional groups present in graphite oxide. The epoxy spectral peak disappeared upon heating the samples or reacting graphite oxide with NaOH, which preferentially attacks the epoxy groups. These processing steps did lead to a significant hydroxyl group FT-IR signal. DC magnetic susceptibility measurements with a SQUID magnetometer fit to a Curie-Weiss law provided negative Curie temperatures, indicating the presence of antiferromagnetism with an effective Bohr magnetic number ranging from 0.17 to 0.28 depending on applied field. The heated and NaOH treated samples, in contrast, exhibited paramagnetic behavior. Lee et al. proposed that a superexchange interaction between epoxy groups could lead to antiferromagnetism, but other mechanisms are possible, and additional experimental and theoretical work is needed to help resolve this issue.

A recent theoretical work based on density functional theory has also indicated that graphene nanoribbons functionalized with an epoxy chain could be magnetic [134]. Based on energetic analysis, they find that graphene nanoribbons with a central epoxy chain should be energetically favorable. Similar to previous studies [135, 136], they find that zigzag graphene nanoribbons have an antiferromagnetic ground state. With the addition of a central epoxy chain, the nanoribbon ground state becomes ferromagnetic with magnetic moments situated primarily on the nanoribbon edges and along the epoxy chain. This model however does not explain a recent experimental study of magnetism in graphene oxide nanoribbons prepared by chemically unzipping carbon nanotubes [137] that found evidence of paramagnetism. In this case, placement of functional groups on the surface is disordered and suggest that the paramagnetic behavior could be due to the presence of carbonyl functional groups.
at the edge of the graphene nanoribbons. The lack of agreement between theory and experiment could be due to this disorder. Wang and Li do note that calculations based on random epoxy groups do not lead to a magnetic state. Another explanation could be that the oxidized nanoribbons formed from carbon nanotubes do not possess a large number of epoxy groups or also include hydroxyl groups that prevent the formation of epoxy chains.

1.7 Future Perspectives

In this chapter, we have examined the atomic structure, electronic properties, and fabrication of graphene oxide, as well as some of its possible applications. Of all the functional forms of carbon that are currently under consideration, a clear understanding of the chemistry and physics of graphene oxide is perhaps the most critical for the birth of a graphene-based electronics industry. It is important to remember that the phrase graphene oxide actually encompasses a fairly wide range of oxidized graphene structures that possess a range of C:O ratios and that can be fabricated using a variety of techniques. Current research strongly indicates that functional groups on the graphene oxide surface are for the most part randomly distributed and that the insulating properties of these materials depends strongly on the amount of oxidation. While there is limited evidence of ordered oxygen functional groups on a graphene surface, it remains to be seen whether careful growth conditions could lead to crystalline forms of graphene oxide. For the use of graphene oxide as a precursor for graphene sheets in industrial settings, the critical issue remains of how to effectively reduce graphene oxide to enhance mobility. Clear evidence exists that oxygen functional groups and defects remain after reduction. The development of processing steps that help the graphene lattice heal during this process will be crucial for the development of viable large scale manufacturing processes.

However, even without the motivation of graphene electronics, graphene oxide shows great promise for a number of industrial applications in its own right. As we have highlighted earlier in this chapter, graphene oxide has shown encouraging results as an charge trapping layer for memory storage devices. Due to its large surface area, reduced graphene oxide can also be used to make competitive capacitors. Transparent reduced graphene oxide sheets could also provide a cheap alternative to the expensive indium tin oxide used in panel displays. Finally, the ability to tune the electronic properties of graphene oxide from insulator to semiconductor to semi-metal provides an important way to chemically define devices and circuits. It is clear that graphene oxide is an unique and promising material that requires further understanding and that should benefit progress in a number of fields.
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