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GRAPHENE OXIDE SYNTHESIS AND RADIOLYSIS

A Thesis in

Materials Science and Engineering

by

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ABSTRACT

The diverse functionalization of graphene oxide (GO) provides this material unique chemical and physical properties that can theoretically be tailored during the synthesis and/or reduction of the material. One specific property of interest for the opto-electronic industry is the ability to tailor the optical band gap of GO, which can be modified by selective functionalization or through the formation of heterogeneous structures. Understanding the mechanisms through which this functionalization can be controlled is necessary before GO can be implemented into these opto-electronic devices.

This thesis investigates the effects of the synthesis process on the GO structure; identifying key parameters for the oxidation method, cleaning procedure and starting material selection. It is determined that water significantly affects the present functional groups in GO. Also the size of the GO flakes correlates with the crystallite size of the graphite material, as well as the starting flake size. The stability of this structure is then explored through the use of in-situ x-ray techniques. A range of photon radiation sources are used for the in-situ measurements to identify the rate of interaction as a function of photon energy as well as the interaction mechanisms. Lastly, the interaction of GO with other ionizing radiation, such as neutron and alpha particles, is investigated.

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LIST OF ACRONYMS AND NAMING SCHEMES

GO – Graphene Oxide

GO4 – Specific reference to a synthesized graphene oxide material are labeled GOX, where X is the GO run number. Reference Table 13 for all parameters of each GO run.

TOD – Threshold oxidation

- STD Standard deviation
- RSD Residual standard deviation
- D_{AR} Dose Absorbed Rate
- LET Linear Energy Transfer

R1, R2, R3, R4, R5 – The short hand for identified regions in both the carbon 1s and oxygen 1s XPS spectra. Reference Figure 52 for specific functional groups found in each assigned region.

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CHAPTER 1 – INTRODUCTION

Although the oxidation of graphite has been studied for more than a century,¹ a complete understanding of the graphite oxide structure,^{2,3,4} chemistry,⁵ and properties^{6,7} continues to be explored. The comprehensive knowledge of this material continues to elude scientists because the structure is a non-stoichiometric compound dependent upon synthesis method and begins decomposing at around 60-100°C. ^{8,9,10,11,12} This thesis further explores these two subjects by experimentally investigating the effect different parent graphite materials/ synthesis methods have on the structural properties of the oxidized material, and the radiation sensitivity/interaction of the oxidized material as a function of energy and irradiation environments.

1.1 MOTIVATION

The tunable opto-electronic characteristic of GO provides the light-emitting, bio-sensing and non-linear optics communities with a means to target individual species of interest.⁷ Additionally, GO's compatibility with common polar solvents (water, dimethyl formamide, tetrahydrofuran etc.) allows for facile integration with the solution processing required for most opto-electronic applications.⁵ Both of these features in GO are controlled by the amount, type and positioning of functional groups that are present in the structure.¹³ The effect of the functional group on the optical energy gap has been shown through theoretical calculations by Johari et. al., ¹⁴ and is shown in Figure 1.



Figure 1 - Pristine graphene has an optical band gap ~4eV for the π - π * transition (a) and when oxygen functional groups are added to the system the optical band gap is altered (b).¹⁴

An additional way of altering the optical energy gap of the material is by changing the sp^2 domain size (or crystallite size).¹⁵ Increasing the size of the sp^2 domains increases the absorption range for the material and is one cause for the brown color of the GO material.¹⁶ So two primary avenues for tailoring the band gap of GO material is through controlled functionalization and recovering the conjugated π -domains. If the most influential processing steps for the GO structure/chemistry can be identified and understood then fine-tuning for these varying applications can be optimized.

Additionally, it is imperative to understand how GO will behave in some of the common environments that opto-electronic devices are exposed to in order for integration to be successful. Identifying the mechanisms for electromagnetic radiation, heat, and water interaction with GO can provide a route to quantify the meta-stability of GO. Understanding these principles will not only allow for GO incorporation into optoelectronic devices, but could potentially be used to tailor new device systems.

1.2 BRIEF HISTORY OF GO

The earliest known study for oxidizing graphite occurred in 1859¹ and it was determined the resultant structure was quite unique. Very few papers throughout the following century focused on applications of the material, but upon entering the later 20th century

researchers began exploring the electrochemical properties of the graphite oxide material. ^{17,18} A surge in graphite oxide research occurred after it was discovered in 2004 that a single layer of graphite had extraordinary electrical properties¹⁹ and that graphite oxide was a cheap means to synthesize single layer graphite.²⁰ This single layer graphite material is referred to as graphene and this has led to those working on the oxidation of graphite to call their material graphene oxide. This arbitrary term has led to minor confusion, therefore this thesis refers to bulk graphite oxide (BGO) that is greater than one layer and material referred to as graphene oxide (GO) is material that is separated into individual single layer sheets.

The BGO studies in 2004 were focused on the conversion from GO to a reduced graphene oxide (rGO) to determine if the pristine graphene structure can be re-established.^{21,22} During this process, it was realized that GO may have inherent properties that could be utilized for other unique applications. Some of these new applications include hydrogen storage,²³ nano-filtration membranes,²⁴ fluorescent DNA-tagging,²⁵ humidity sensors,²⁶ tunable opto-electronic devices,⁶ absorbing radio-nuclides,²⁷ reducing E. Coli bacterial growth,²⁸ surfactant for otherwise insoluble materials (ex. carbon nanotubes),²⁹ and in polymer composites³⁰ for improving elastic modules, tensile strength and thermal stability. The wide variety of GO applications primarily depends upon the unique chemical structure of the material. Identifying the mechanisms that lead to this unique structure could make GO integration into industry a feasible reality. However, understanding this structure is something that requires significant effort and this is explained in the following sections.

1.3 GRAPHENE OXIDE STRUCTURE

1.3.1 Structure Models for GO

The challenge of understanding the structure of synthesized GO materials through the combination of theory and empirical studies is an ongoing struggle. There have been many iterations of the theoretical GO model, with which have come new insights as well as some

new developments that contradict previous theories. A general consensus has been reached on the types of oxygen functional groups that appear on the GO structure, however their position, percentage and ordering require further investigation. ^{4,31} The most probable functional groups in the GO system are the epoxide (C-O-C) and hydroxyl (C-OH) moieties. ^{5,31,32,33} One of the most referenced theoretical models for the GO structure is a paper written by Lerf et. al.,³¹ and presents an amorphous non-stoichiometric structure (Figure 2). Using reactive agents with GO, the individual functional groups were tagged and recognized in carbon-13 magic angle spinning nuclear magnetic resonance (¹³C MAS NMR). ³¹



Figure 2 - Proposed models for GO from Lerf et. al.,³¹ showing both hydroxyl (C-OH) and epoxide (C-O-C) groups on the basal plane of GO. Model (a) ³¹ proposes carboxylic acid (O-C=OH) along the edge plane while model (b)³⁴ shows the absence of carboxylic groups.

Similar moieties were identified using solid-state NMR by first synthesizing ¹³C graphite material, oxidizing the material and then measuring the material system as a whole without the need for individual reactive agents to isolate suspected groups (Figure 3a). ^{33,35} Other suggested GO structural motifs are carboxylic acid groups (O=C-OH) and carbonyl groups (C=O), primarily along the edge planes. ^{12,31} However, there is less conclusive evidence for these structures and therefore disagreement over their presence as highlighted in the two presented GO structural models in Figure 2. There are two probable reasons for the inconclusive evidence of carboxylic acid and carbonyl groups: 1) certain techniques require elaborate deconvolution (such as FTIR¹¹ and XPS²¹) to determine their presence that may lead to inaccurate conclusions, and 2) research groups do not utilize the same GO synthesis, causing the GO chemistry to vary from one research group to another.



Figure 3 - Solid state NMR of GO using 13C graphite (a), ³⁵ which shows the presence of hydroxyl and epoxide groups in GO and FTIR image (b)¹¹ suggesting the presence of hydroxyl, epoxide, carbonyl and carboxylic groups.

Analysis of GO chemistry through IR spectroscopy often yields a peak with vibrational frequency \sim 1730cm⁻¹ (Figure 3b) and is often assigned to represent carboxylic acid.^{32,36} However, this peak can be representative of a multitude of carbonyl species³⁷ and therefore it is required that multiple characterization techniques are used to identify that it is present in the structure. One attempt to de-convolute the complexity of the FT-IR signal is made by Chowwolla's group¹¹ where they demonstrate the variety of possible structures that each highlighted region could represent. A more general list of carbonyl compounds that are possible candidates for oxygen functional groups present in GO are presented in Table 1. The vibrational energy region selected is the same highlighted region shown in the FT-IR from Chowwolla's group (Figure 3b). Even XPS measurements of the GO material can be ambiguous due to the convolution of so many chemical shifts in the emitted photoelectrons from the carbon 1s orbital. What is rarely shown is an in-depth study of both the carbon 1s and oxygen 1s orbital photoelectron peaks to re-confirm the peak assignment of a carboxylic group. The value of confirming or denying the presence of carboxylic acid in the structure is to determine if this presence is the cause for such an amphiphilic character in the GO material³⁸, which will be discussed later.

Table 1 - This chart shows the location of IR vibrational peaks for candidate carbonyl compounds in GO in a specifically convoluted region in the IR spectra. The line for each compound represents the regions where the peak can be found and the label (m or s) represents the intensity of the signal (medium or strong). Information is adapted from Socrates (1980).³⁷

	1450	1400	1350	0 13	300 12	250 12	200 11	.50 1:	100 1	050 10	00 950
Carbonyl Compound											
ketones		m-s	_				s				
quinones	m			m		m		m		m	-
anhydrides								m-s			
carboxylic acid				m	-s			s			
ester					S				m-s		
	nie Miller				former and a second		-			2	

First-principle calculations suggest several models of GO with completely ordered grouping of the epoxide and hydroxyl groups throughout the basal plane. ^{39,40} These reports propose a long-range order with chain like structures of epoxide and hydroxyl groups on both sides of the sp² graphitic domain. However, this long-range order of functional groups has not been shown in any empirical study to date. With the advance of aberration corrected high resolution TEM measurements, some groups have shown in great detail (Figure 4) that the GO structure is nonhomogeneous with areas of oxygen functionality, surrounding pockets of pristine sp² graphite and even some holes. ⁴¹ One explanation for this phenomenon is derived through density functional theory (DFT), which shows that the oxidation process nucleates from thermally stable oxygen sites until functionalized areas grow to a size where oxygen mobility is more favorable than further oxygen adsorption. ³ This may help explain why the functionalized areas form a network around pristine sp² graphite regions as shown in the TEM image of synthesized GO material (Figure 4).



Figure 4 – This ultra high resolution TEM using aberration corrected lens image highlights the presence of oxygen moieties/sp³ bonding (a), individual hydroxyl/epoxy groups (b), sp² graphitic domain (c) and holes in the GO structure. The scale bar is set to 2nm.⁴¹

This growth mechanism for the functionalized area may also help explain the threshold oxidation degree (TOD) that is seen in all empirical studies of the GO material as well. From the literature these TOD C:O values range from 1.8-2.5, however most average \sim 2.0. ^{1,} ^{12,42,43,44,45} It is important to understand the type and quantity of these functional groups, because it is this structure that can dictate the electrical behavior⁴⁶ and optical sensing⁷ of the GO material.

1.3.2 GO Chemistry and the Influence of Synthesis Process

The generation of intercalation compounds in graphite has been accomplished through many chemical reactions, and with the use of a variety of compounds (Table 2).⁴⁷ However, there are only two compounds used that form covalent bonds to the graphitic skeleton: fluorine and oxygen. In the covalent bond the graphitic carbon is the donor and the oxygen functional group adsorbate is the acceptor, therefore the electrical conductivity of the material is reduced as the adsorbate coverage is increased. The presence of the oxygen has also been shown to affect the acidity and amphiphillic nature of the GO material system.¹² However, the exact mechanism causing a change in the pH-dependent amphiphile is not

completely agreed upon and is explained in the following paragraphs.^{48,16}

Table 2 - A list of some possible intercalation compounds that can be added to graphite and the
limiting composition

Intercalate	Limiting Composition	Reference
02	C ₂ O, C ₄ O ₂ , C ₄ O, C ₈ O, C ₁₂ O	40
F ₂	$(CF)_n, (C_2F)_n, C_4F$	47
Li	C ₆ Li, C ₁₂ Li, C ₁₈ Li	47
Na	C ₆₄ Na	47
K, Rb, Cs	C_8M , $C_{24}M$, $C_{36}M$, $C_{48}M$ (M = K, Rb, Cs)	47
H ₂ SO ₄	C ₂₄ *HSO ₄ *H ₂ SO ₄	47
HNO ₃	C ₂₄ *NO ₃ *3HNO ₃	47
HF	$C_{24}*HF_{2}*2H_{2}F_{2}^{47}$	47

The carboxylic functional group on GO is a weak acid, which appears on the edge of the carbon plane. The primary functional groups along the basal plane are hydroxyls and epoxides, which are weak acids and non-acidics, respectively. This separation of functional groups generates varying localized pH values in the system. Some have hypothesized that it is the separation of acidity that leads to the amphiphilic nature of GO.⁷ Thus, controlling the long-range and short-range order of the functional groups not only affects the TOD (as mentioned in section 1.3.1), but it could also affect the amphiphilic properties of GO.

By tailoring the pH of the GO in a solvent it has been shown (Figure 5) that this changes the surface potential interaction with a solvent, which can alter the electro-static double layer capacitance (EDLC) between particle and solvent.³⁸ The EDLC is what dictates the strength and stability of a colloidal suspension and is determined by both the ionic strength in the system as well as the surface potential. The suggested surface charge in GO is via the dissociation of carboxylic acid and hydroxyl groups.⁴⁸ Therefore, it is possible that

controlling the ratio of carboxylic acid groups and in-plane hydroxyl groups is one method for adjusting the overall stability of GO in a suspension. However, it is important to note that this is one of many possibilities to alter the surface potential of the colloidal system.⁴⁹



Figure 5 – pH-dependent amphiphilic nature of GO is determined by the dissociation of the carboxylic acid group (a). When placed into different pH environments (b-e) of a toluene-water mix (toluene on top, water on bottom) the quality of the suspension alters. In the base suspensions (b & e) the material is deprotonated and more hydrophilic, therefore forming a better suspension in water. As the pH is lowered to 5 (c) there is a greater interaction at the oil-water interface because the material is protonated, therefore becoming hydrophobic. At the pH of 2 (d) the GO is completely extracted from the water to form the water-oil interface. The interfacial tension (γ) decreases as the pH decreases, which further verifies that the amphiphilic nature of GO is pH-dependent.⁴⁸

Another theory for this pH-dependent amphiphillic nature of GO determined that carboxylic acid is not the influential species.¹⁶ Dimiev et. al.,¹⁶ propose that most papers reference a GO material with an edge to basal plane ratio of 1/10000 and if that is the case, then the minute amount of carboxylic acid (which only forms along edges) could not affect the pH as greatly as is measured after oxidation of the material. ¹⁶ Instead Dimiev et. al.,¹⁶ suggest that incomplete hydrolyzed covalent sulfates remain in the GO material system after the purification process. Dimiev et. al.,¹⁶ investigate two materials: one GO system was oxidized using the Tour method⁹ with no aqueous solution added to the system during cleaning, while the second GO was oxidized and then cleaned in the standard HCl, ethanol, DI water rinses. The first GO material system was washed using a variety of non-aqueous solutions including methanol, glacial acetic acid, trifluoroacetic acid, ethyl acetate and isopropanol. It was determined that sulfur-containing impurities remain in all GO samples,

even up to 2% in water washed samples. Using FTIR, it is suggested that the sulfurimpurity is a covalently bonded sulfate and Figure 7 presents proposed mechanisms by which this sulfate is formed.¹⁶



Figure 6 - The formation of the covalent sulfate bond occurs through nucleophillic attack of sulphuric acid at epoxide sites(1). The sulfate ester (2) then attacks neighboring epoxide, forming two hydroxyl groups and one 1,2-cyclic sulfate (3). Hydrolysis then occurs with the addition of water (4). The removal of the sulphuric acid during water rinses occurs faster than the hydrolysis of the covalent sulfate and both reactions are slower in an acidic environment. As seen in step (5) of the schematic, the product of covalent sulfate hydrolysis is the formation of sulphuric acid. ¹⁶

When water is added during the standard cleaning process of GO, the covalently bonded sulfate hydrolyzes to form sulphuric acid, which could help explain the acidic nature of GO (Figure 6).¹⁶ The half-life for the covalent sulfate hydrolysis is ~15hrs when in an acidic environment, and significantly reduced for basic environments.¹⁶ This slow reaction may explain why sulfur is often found in the elemental analysis of GO.^{22,50} This proposed mechanism also suggests that after these 1,2 diols are formed in step (5) of Figure 6 that the addition of water can cause the conjugated areas to re-heal and enhance the GO acidic nature by converting tertiary alcohols into ketones, shown in step 8 of Figure 7.¹⁶ Therefore, it is suggested that the cleaning procedure can have just as great an effect on the chemistry and structure of GO as any of the oxidation parameters.



Figure 7 - One 1,2-diol fragment (6) left from the hydrolysis of 1,2-cyclic sulfate ionizes and the other cleaves the C-C bond (7) with the formation of ketone and enol. During this step one hydroxyl group is removed and one C=C is formed, causing the conjugated area to extend. The enol (7) ionizes with formation of one or more double bond to form (8).¹⁶

The affect of the cleaning process on the GO chemistry/structure was proposed in 2012.¹⁶ Prior to this discovery, most research focused on the effect of the oxidation process on the GO chemistry/structure.^{5,51} Some variables that are proposed to affect the GO structure/chemistry during the oxidation process are the type and amount of reactants/electrolytes,⁵¹ the length of the oxidation time,¹² and the temperature of the solution during key steps.¹⁶

The two classes of reactants often used for the GO oxidation process are permanganates $(XMnO_4)$, and chlorates $(XClO_3)$. The methods that use these two reactants are summarized in Table 3. Contemporary GO research has focused on the permanganate methods, largely due to the added safety of these procedures. The oxidation using chlorate produces a chlorine dioxide gas, which can decompose via sunlight, UV light, or heat and is violently explosive/toxic at >12%.⁵² Some permanganate methods also pose a safety hazard because they can generate nitrous oxide gas, which is toxic and chronic exposure can cause damage to the central nervous system, however it is ranked less toxic than chlorine dioxide. ⁵³ The most recent method that was proposed by Tour removes all toxic gas formations by omitting the use of the sodium nitrate oxidizer and instead adds phosphoric acid. ⁹

Table 3 - Comparison of the most common oxidation methods for GO, the procedures followed and the threshold oxidation for each method.

Graphite	Reactants and	Experimental Methods	Cleaning Procedure	C/O	Ref
	Electrolytes				
Natural	Fuming HNO ₃ +	NaClO ₃ :Graphite (8.5:1) 60°C	Washed w/ 5x100mL	Run 1:	12
Flake (250-	NaClO ₃ (Brodie	for 8hrs the subsequent GO	HCl and 7x1L of DI	2.60	
500um)	Method)	was then retreated through	water	Run 2:	-
		Brodie method 3 more times		2.20	
		at NaClO ₃ :GO (2.8:1)		Run 3:	-
				2.17	
				Run 4:	-
				2.04	
Natural	H ₂ SO ₄ + H3PO ₄ +	H_2SO_4/H_3PO_4 (9:1) and	Washed w/ water, HCl	69%	9
Flake	KMnO4 (Tour	KMnO4:Graphite (9:1) 50°C for	then ethanol twice.	oxidized	
(150um)	Method)	12hrs, cooled to RT, added to	Then dried on PTFE	carbon ⁱ	
		ice with 0.1% H_2O_2 in water	membrane with		
		solution.	0.45um pore size.		
Natural	$H_2SO_4 + NaNO_3 +$	KMnO ₄ :Graphite:NaNO ₃	Washed w/ water, HCl	63%	9
Flake	KMnO₄	(18:3:1.5) 35oC for 30min,	then ethanol twice.	oxidized	
(150um)	(Modified	water added to produce	Then dried on PTFE	carbon ⁱ	
	Hummers	exotherm 98°C, held at temp	membrane with		
	Method)	for 15min, added to more	0.45um pore size.		
		water with 0.1% $\rm H_2O_2$			
Natural	$H_2SO_4 + NaNO_3 +$	KMnO ₄ :Graphite:NaNO ₃	Washed w/ water, HCl	61%	9
Flake	KMnO₄	(9:3:1.5) 35°C for 30min,	then ethanol twice.	oxidized	
(150um)	(Hummers	water added to produce	Then dried on PTFE	carbon ⁱ	
	Method)	exotherm 98°C, held at temp	membrane with		
		for 15min, added to more	0.45um pore size.		
		water with 0.1% $\rm H_2O_2$			
Natural	$H_2SO_4 + HNO_3$	H_2SO_4/HNO_3 (2.1:1) and	Washed w/ HCl (5%)	2.47	51
Flake	+KCIO ₃	KClO ₃ :Graphite (11:1) flask was	and DI water until pH		
(<20um)	(Staudenmaier	capped and stirred at RT for	was neutral then dried		
	Method)	96hrs, then added to water	at 50°C for 5 days		

Natural	$H_2SO_4 + HNO_3$	H_2SO_4/HNO_3 (3:1) and	Washed w/ HCl (5%)	2.71	51
Flake	+KClO₃	KClO ₃ :Graphite (11:1) flask was	and DI water until pH		
(<20um)	(Hofmann	capped and stirred at RT for	was neutral then dried		
	Method)	96hrs, then added to water	at 50°C for 5 days		
Natural	$H_2SO_4 + NaNO_3 +$	KMnO ₄ :Graphite:NaNO ₃ (6:1:1)	Washed w/ warm	2.05	51
Flake	KMnO₄	35° C for 1hr, water added to	water until neutral pH		
(<20um)	(Hummers	produce exotherm up to 90°C,	was achieved then		
	Method)	held at temp for 30min, added	dried at 50°C for 5		
		to more water with 3% $\rm H_2O_2$	days		
Natural	$H_2SO4 + H_3PO_4 +$	H_2SO_4/H_3PO_4 (9:1) and	Washed w/ water, HCl	1.95	51
Flake	KMnO₄ (Tour	KMnO₄:Graphite (9:1) 50°C for	ethanol and diethyl		
(<20um)	Method)	12hrs, cooled to RT, added to	ether then dried at		
		ice with 0.4% H_2O_2 in water	50°C for 5 days		
		solution.			

i: These papers did not present a C/O elemental ratio, rather the percent oxidized carbon was calculated from peak fitting in XPS In addition to safety, Table 3 shows that the permanganate reactants also yield a GO material that has a greater TOD than the chlorate samples. The method with the greatest threshold oxidation value is the most recent Tour process, with a C/O of 1.95.⁹ Specifically, the permanganate methods showed a higher percentage of carbonyl (C=O) and carboxylic acid (O-C=O) groups when investigated with XPS and NMR techniques.⁵¹ Shao *et. al.*⁵⁴ suggested extended oxidation processes (1.5hrs) at elevated temperature (45°C) causes significant chemical/structural changes, specifically the formation of carboxylic acid.

Another lab group, Szabo et. al., ¹² has also tested extended oxidation time through repeat oxidation steps. This group found that the C/O ratio for material after the initial oxidation was 2.60 and after 3 more repeat oxidation steps the C/O reached 2.04, as shown in Table 3. With each step the percentage of water also increased, starting at 7.7% and finishing with a water content of 11.2%. Therefore, the water had a significant presence in the overall structure. To determine the affect of the oxidized carbon on the inter-layer separation the GO materials were dried completely in a dessicator. Interestingly, the increase in inter-layer separation was insignificant as the repeated oxidation steps were performed. Thus the maximum corrugation effect the covalent oxygen functional groups

have on the structure is reached at lower oxidation levels when performing repeat oxidation steps. However, within minutes the GO material re-hydrated just from the humidity of the air and the inter-layer spacing increased. This study was the first to show that the addition of oxidized carbon after initial oxidation yields little expansion and also solidified the importance of understanding the hydrophilicity of GO. ¹²

The affect of water was further explored by Chhowalla et. al.,¹¹ and determined that water can significantly impact the chemistry of the GO material. In-situ FTIR measurements show that when heating multi-layer GO material there is an increase in formation rate of carbonyl and hole defects in comparison with single layer GO material or material formed with ethyl alcohol (removing water content).¹¹ This suggests that water can promote the formation of oxygen groups and defects during oxidation as well as during the thermal reduction of the material. GO materials with the highest oxidation (Tour method) are cooled to room temperature before adding the acid slurry to ice water and H₂O₂. Shi et. al., ⁵⁵ studied this phenomenon by first oxidizing graphite using the original Tour method and modifying it by adding the acid slurry directly to water after it had been heated to 50°C for 12hrs. Their results showed that the original Tour method increased the oxidation and inter-layer spacing as compared to the modified Tour method. Therefore, the time, amount and temperature of water must be considered as another key parameter during the formation of GO.

In summary, it is known that GO has hydroxyl and epoxide groups throughout the basal plane and it is probable that carbonyl and carboxylic acid groups form along the edge. ^{22,31}, ^{39,41,56} So far, all experimental analysis has shown that these groups are random and have very short-range order, which contradicts theoretical calculations. ^{3,4,39,54} This short-range ordering may also explain why the TOD maximum is ~ 2 .¹⁶ Controlling the TOD value as well as the type, amount and location of the functional groups can vary properties such as the optical band gap and amphiphilic nature of GO.^{21,29,48,55} And the explored methods through which the functionality and TOD of GO can be controlled are the cleaning method, reactants/electrolytes used during oxidation, the length of oxidation, and temperature of

reactions (specifically water addition). ^{12,16,51,55}

1.4 RESEARCH FOCUS

1.4.1 Process/Property Relationship

It is quite evident that the structure of GO can impact many different properties and applications. Specifically, by adjusting the percentage of oxygen, the types of oxygen functional groups, the arrangement of these groups and the size of each domain yields a material with uniquely different behavior optically and chemically. The goal of this research is to continue to investigate the oxidation process variables by studying what impact the starting graphite material has on the subsequent structure and chemistry of the oxidized product. Three starting materials were selected for this study based on the current use and ability to up-scale production of GO using the selected graphite materials, because having a scalable and optimized process for GO is the end goal. The graphite materials include expanded flake graphite, synthetic graphite and natural flake graphite. Each one of these is a uniquely different material with varying starting chemistry and structure. They are also materials that are available on large scale. Each of these materials were synthesized to form GO using the newly developed Tour method⁹ as well as the most commonly referenced Hummers method⁴². Additionally, parameters related to the liquid exfoliation process were studied in order to determine their affect on the overall structure. The synthesized GO through Tour method yields $C/O \sim 1.8$, which is uncharacteristically low even for this new method. An extended cleaning procedure is performed, which is one explanation for the dramatically high level of oxidation in the structure. The parent material also had a large impact on the physical morphology of the GO material as well as varying chemistry.

1.4.2 Radiation interaction/reduction of GO

Another interesting discovery during this study was that overtime, dried GO material held
at RT conditions in closed containers changed chemically. This was further explored by testing the reduction of GO in a variety of environments. It was known that GO could reduce under mild thermal conditions, as low as 60°C,⁸ but the interaction with electromagnetic radiation was less known. Consequently, a variety of ionizing radiation sources were exposed to GO ranging from high energy photon interaction to nuclear radiation and ion bombardment. These irradiations were all executed in-situ using XPS (excluding neutron irradiation measurements), avoiding contamination for extraneous light sources as well as environmental conditions. Studies were initially performed to determine what affect the x-ray source had on the GO chemistry and a correction value was calculated. The dose energy and interaction probability of each radiation source was normalized and it was determined that the change in chemistry of GO varied for each source. Using X-ray Excited Optical Luminescence (XEOL) the photolysis cross-section for GO during x-ray exposure was calculated.

CHAPTER 2 – GO SYNTHESIS

2.1 INTRODUCTION

2.1.1 Graphite Material

In the following pages, the effect of starting material on graphite oxide (GO) using the two most prevalent methods in the field (Hummers⁴² and Tours method⁹) will be explored. Selection of the starting material was based upon: availability, price, distinctly unique chemistry, and flake size, which lead to the use of two natural graphite materials (macrocrystalline flake and expanded flake) and one synthetic graphite powder. Those materials selected are shown in Figure 8 and are highlighted in a red outline.



Figure 8 - Classification for varying types of graphite materials showing those materials selected for this study (highlighted in red box).⁵⁷

Each of the selected materials: natural flake,^{9,12} expanded flake (or intumescent flake),^{58,59} and synthetic^{48,60} have been used as the starting material for GO synthesis previously, but never compared in one comprehensive study to understand their direct affect on GO chemistry and structure. Typically natural flake graphite is used for GO synthesis,^{9,61} however most recently researchers have investigated the use of expanded flake material,

which has an intercalating compound. Graphite materials that were omitted from this study were materials that are not economically feasible for large scalability of GO production, had maximum size limitations at sub-micron, or did not provide a unique chemistry from those selected.

2.1.1.1. Crystal Structure of Graphitic Starting Material

Graphite has been used for centuries for a variety of applications and the structure of graphite has been well documented. Most structural properties are true for all graphite materials; however some qualities of the structure and chemistry are often tailored to best fit certain applications, such as the morphology, surface area and purity. All graphitic powders used in this study were acquired from Asbury Carbons Inc where Table 4 describes the powder properties.

Table 4- Information provided by the Asbury Carbons supplier for each graphite material used in this study

	Natural	Natural	Synthetic		
	Graphite -	Graphite -	Expanded	Graphite – Micro	
	3243	3763	Graphite - 3772	450	
Crystal	Hexagonal	Hexagonal	Hexagonal	Hexagonal	
System	пехадона	пехадона	пехадона	nexagonal	
Crystal Class	6mmm	6mmm	6mmm	6mmm	
(H-M)					
Space Group	P6₃/mmc	P6 ₃ /mmc	P6 ₃ /mmc	P6₃/mmc	
	{0001} - basal	{0001} - basal	{0001} - basal	{0001} - basal	
Crystal Planes	{1010}-prism	{1010}-prism	{1010}-prism	{1010} prism	
	{1011}-	{1011}-	(1011) pyramid	(1011) pyramid	
	pyramid	pyramid	{1011}-pyrannu	{IOII}-pyrainiu	
Morphology	Flake (lamella)	Flake (lamella)	Flake (lamella)	Flake (lamella)	
Specific					
Gravity	2.26 <u>+</u> 0.02	2.26 <u>+</u> 0.02	-	2.28 <u>+</u> 0.02	
(ρG/ρW)					
Metling Point	2652±10	3657±10	3652±10	3652±10	
(°C)	5052 <u>-</u> 10	5052 <u>1</u> 10	5052 <u>1</u> 10	5052 <u>1</u> 10	
Flake Size	44-75 (26%)	425-500 (79%)	250-300 (49%)	< 5 (90%)	
(um)	44 73 (2070)	423 300 (1370)	230 300 (4370)		
Surface Area	3 15	_	_	17 33	
(m2/g)	5.15			17.55	
рН	-	-	6.61	-	
Carbon %	99.5	99.6	97.9	99.2	
Moisture %	-	0.16	0.92	0.24	
Sulphur %	-	-	3.1	-	

The graphite structure exhibits AB stacking, where the primitive unit cell consists of 4 atoms, labeled A, A', B and B' in Figure 9. Although both A and B atoms have a similar coordination number of 3, the distinction between the stacking planes is that the A and A' atoms are directly in-line along the z-direction at a distance of 3.35 Å (half of the total c distance), where as the B atom has 12 symmetrically distributed next nearest neighbors at an equal distance of 3.70 Å. ⁶²



Figure 9 – The AB stacking in graphite (a) has an interlayer spacing of 3.35 Å and C-C bond length of 1.42 Å (distance from A to B in xy-plane). The dimensions of the primitive hexagonal unit cell are a=2.46 Å (distance from A to A atom along the xy-plane) and c=6.71 Å (distance from B to B along the yz-plane). The crystallite dimensions (b) Lc and La are used to characterize the size and shape of the graphite crystal structure. ⁶³

2.1.1.2 Natural Flake

Natural flake graphite is the most prevalent form of graphite, with large deposits located throughout North & South America, Africa, Germany, Ukraine, Russia, and China. The graphite content from the ores mined from these deposits is often very low (5-40%) and requires separation and purification techniques. Naturally occurring impurities in the graphite structure often are mechanically bonded mineral grains that have been cold welded through pressurization over time and 'intercalated' ash between parting layers of graphite. These impurities require significant purification not often performed for

commercial grade graphite (80-99.5%). To exceed purity values of 99.9%, high temperature treatments are often required for the graphite.⁴⁷

Natural flake graphite retains its flake morphology (also referred to as lamella morphology) at all sizes and can range from sub-micron domain size up to one millimeter. The size of the flakes depends upon the amount of milling and grinding throughout the extraction and purifying procedures.⁵⁷

2.1.1.3 Expanded Natural Flake

One particular form of flake graphite that has been used recently in GO production is expanded graphite. It is advantageous because it already has an intercalated layer, which helps weaken the van der Wall forces that hold the graphite crystal layers together. The chemical species used for the expanded graphite material are strong acidic anions. The material used here is an expandable graphite material with a bisulfate intercalation layer. When the graphite is plunge heated (~800°C), it can cause the material to expand by a factor of 300. The material is then wet milled down in a water slurry to a fine powder with an average thickness of about 100nm. The plunge heating process was not performed in this study. Instead, the interaction of this expandable graphite material with the Tours⁹ and Hummers⁴² oxidation was investigated. It is already known that the bisulfate species do not induce significant expansion until the expandable graphite reaches a temperature of 180°C.⁵⁷

2.1.1.4 Synthetic

Synthetic graphite constitutes graphite that requires processing and heat treatment (above 2500°C) of raw materials to form the graphitic structure. There are many different types of raw materials and heat processes that yield graphite with varying characteristics and morphology. One common attribute for all synthetic graphite is that none of these have macro-flake morphologies like natural graphite. It is only until the structure of certain synthetic graphite is ground very finely (~5um) that it shows flake morphology. The synthetic material in this study is synthesized via graphitization of petroleum coke. This method requires the coke material to be mixed with coal-tar pitch and heated to 1000°C to

expel volatile constituents. The resulting material is amorphous carbon, still consisting of petroleum coke particles, requiring heat treatment at 2500°C – 3000°C to convert it into a graphitic material. Synthetic graphite is often used for electrochemical applications due to the high purity of the material. ⁴⁷

2.2 EXPERIMENTAL

2.2.1 Synthesis

2.2.1.1 Hummers Method⁴²

The following describes details pertaining to the Hummers method⁴² utilized in this work. The process was performed under fume hood (rated at 128 ft/min). Graphite powder, sodium nitrate (NaNO₃) and sulfuric acid (H₂SO₄) are mixed into a 1 L beaker. Subsequently, the beaker was set in an ice bath and potassium permanganate (KMnO₃) was added to the suspension slowly to prevent the mixture from heating above 20 °C. The ratio between the powder materials (KMnO₃:Graphite:NaNO₃) was 6:2:1. The addition of KMnO₃ causes an exothermic reaction, which separates graphite layers. The mixture is heated to 35 °C and stirred using Teflon coated stir bar (800 rpm) for 2 hours. Subsequently, a DI water/H₂O₂ combination was added to the suspension, causing effervescence and an increase in temperature to ~90 °C. The final suspension was a golden brown suspension.

2.2.1.2 Tour Method⁹

The procedure for the Tour method⁹ began with a 9:1 mixture of concentrated sulfuric acid : phosphoric acid ($H_2SO_4:H_2PO_3$). Then KMnO_4 and graphite (9:1) were slowly added into the concentrated acid mixture in a 1 L beaker. The addition of the oxidizing agent caused an exothermic reaction 38-44 °C, and was immediately placed on a hot plate to at 50 °C and stirred for 12 hours. Although this reaction does not out gas the toxic ClO₂ as in the Hummers method, it was still performed in a fume hood. After the 12 hours the suspension was cooled to room temperature before pouring onto ice and H_2O_2 (0.1 % in water). The final suspension was purple.

Chemical Materials used for Tour and Hummers Method					
Material	Supplier & Purity				
Graphite Powder	Asbury				
Sodium Nitrate (NaNO3)	J.T. Baker, crystal				
Phosphoric Acid (H ₂ PO ₄)	J.T. Baker 85% concentration				
Sulfuric Acid (H ₂ SO ₄)	J.T. Baker 93% concentration				
Potassium Permanganate (KMnO ₃)	J.T. Baker				
Hydrogen Peroxide (H ₂ 0 ₂)	J.T. Baker 30% concentration				

Table 5 - Information on the materials used in the Tour method⁹ and Hummers method⁴².

2.2.1.3 Cleaning

Two cleaning procedures were used to remove residual ions from the oxidation process. The first method was a filtration process using a coarse fritted filter, which retained particles >40 μ m and flutted filter paper with a particle retention size of 30 μ m. The GO was removed from the acid slurry mix by passing the suspension through this filtration system. The material was then rinsed with water by passing water through the captured GO material that lay on top of the filter paper. The amount of water used for this step was 40 ml for every gram of graphite that was used in the oxidation run. The flow rate of water through this GO/fritted filter was very slow and a rotary pump had to be used to pull the suspension through. This initial rinsing step could take up to 2 days, even with the pump. Then HCl (5% concentrate) was poured through the GO/fritted filter to remove the manganese ions remaining in the GO material. The amount of HCl used for this step was 80 ml for every gram of graphite that was used in the oxidation run. This was the final step in the filtration cleaning method and Figure 11 shows the material after the HCl rinse. This method can require weeks to accomplish, and as more runs were performed the flow rate of the suspensions decreased to the point where the system became completely clogged. The fritted filter was cleaned after each run using warm piranha solution (sulfuric acid and hydrogen peroxide), but it could not remove all organics in the filter, resulting exploration of a new cleaning method.



Figure 10 - Cleaned GO material using the filtration cleaning method showing the GO stacked on top of the fritted filter.

The second cleaning method used centrifugation to separate the GO material from suspension. The suspension was centrifuged in sterile 50ml test tubes that are rated for 20,000 rcf (relative centrifugal force). The final acid suspension after the oxidation process was stirred (due to settling of majority of the particles) and then poured into the centrifuge test tubes. These suspensions were then centrifuged at 6000 rpm for 20 min. Following centrifugation, the supernatant was decanted and the mass precipitate material was measured. To begin the removal of sulfur compounds and magnesium ions, 40 mL of water was added to the precipitate in each test tube. The pH of this material was then measured using an EcoSense® pH10A meter with double junction electrode until the meter settled on a value for a minimum of 20 seconds. This suspension was then centrifuged at 4000 rpm for 10 min and the supernatant was once again decanted away. This same procedure was performed for 30 mL of HCl (30%) added to each tube and 30 mL of Ethanol (Reagent Alcohol) added to each tube, however no pH measurements were made after the addition of either of these suspensions. After repeating the water, HCl and ethanol cleanse a second time, the precipitate went through repeated water cleansing steps (up to fifteen times for one test tube). GO material was run through this water rinsing step until the pH reached a minimum value of 4. Following this cleansing the GO suspension was ready for the sonication process.

2.2.1.4 Final Product

The GO was analyzed in multiple forms: as a suspension, powder, thin-film (deposited on substrate) or as free-standing paper (300 – 30000 nm thick). To form the suspension, GO in water would be centrifuged once more after the ultrasonication. Once again the supernatant was decanted away, and this time methanol was added to the suspension. The suspension was lightly ultrasonicated again for 5 min, followed by centrifugation. Most of the supernatant was decanted away, again retaining some of the methanol:water suspension and more methanol was added. This was performed until the suspension was 9:1 methanol:water.

To form GO powder the initial ultrasonicated suspension was filtered using a coarse glass fritted filter (25-50 μ m) and medium filtration paper (10-20 μ m) placed on top to suppress damage done to filter and increase the amount of powder retrieved. The powder was then removed and dried under vacuum at ~100 mTorr for a minimum of 12 hrs.

In a similar fashion the GO suspension was dried out onto polytetrafluoroethylene (PTFE) sheets in a fume hood to form a GO paper material. The lateral size of the GO paper was limited only by the amount of GO suspension prepared and the size of the PTFE sheet. Once the material was dried, an additional layer of GO suspension was dropped over the dried GO. This step was repeated a minimum of three times (otherwise material was too thin to remove from the PTFE sheet) and directly affects the thickness of the GO paper. After the GO material was dried the paper is easily peeled off of the PTFE sheets. The thickness variation of the GO paper was from $0.3 - 60 \mu m$.

All GO thin films are deposited via spin, drop, or spray casting. GO samples were spun deposited onto silicon wafers, which had been cleaned/prepped using an organic solvent clean (Acetone, IPA and DI water) and plasma O_2 -Ar ($O_2 - 10$ sccm, Ar – 40 sccm) etch. The plasma etch was performed in a Plasma Therm 720 at 10 mTorr for 30 seconds with a power of 200 W. If deposited onto Si O_2 , only an organic solvent clean was necessary due to the significant presence of an oxide layer in Si O_2 . Spinning the suspension onto Si O_2 /Si was performed using a resist spinner at 4000 rpm and 0.5 μ l/mm² were dropped at a time onto the substrate. The drop casting was performed on GaN, Al₂ O_3 , Si and Si O_2 substrates,

covering the surface with the suspension and allowing the solvent to dry off over short period of time. Another method used to deposit GO suspension onto substrates was a spray casting technique. Spray casting was accomplished using an airbrush and conveyor belt system, allowing for air pressure, air speed, aperture size, scanning speed, and spray height to all be controlled. Spray casting was performed on GaN, Al₂O₃, Si and SiO₂ of varying shapes and sizes.

2.2.2 Morphology Characterization

2.2.2.1 Atomic Force Microscopy (AFM)

A Digital Instrument 3100 AFM in tapping mode was used to characterize GO thin films. Images were captured at 512 pixels/line and the scanning speed varied from 0.1-2 Hz depending on scan size and surface roughness. Any image that was 10x10 μ m or larger was captured at a scan speed <0.7 Hz. When running samples, the real-time channels that were captured were height data and the phase data. The tip used for the scans was from Nanosensors (PPP-NCH-W Si tip). It was n+ Si with resistivity of 0.01-0.02 Ω -cm, resonance frequency 204-497 Hz and force constant of 10-130 N/m. When analyzing the images a second order plane fit was used to compensate for the bowing effect during measurements, which is an instrumental effect. When determining step height of individual GO flakes, an averaging section analysis was performed. This specific section analysis averaged the height profile of two parallel lines of data, which could be drawn anywhere within the captured image. Using this height analysis tool allowed the user to better represent the height profile and subsequently the thickness of the GO flake. ImageJ was used to analyze the lateral dimensions and total area of each individual GO flakes.

2.2.2.2 Scanning Electron Microscopy (SEM)

The SEM used for the work presented here was a Leo 1530 FESEM with a GEMINI electron column. GO samples had to be run at low voltages at around 1 kV, due to insulating characteristics and sometimes required the use of some conducting metal sputtering (either gold or iridium). The GO samples were imaged as a thin-film spin deposited onto Si

substrate as well as free-standing paper. The GO paper was mounted orthogonally to the electron beam so that the thickness of the paper material could be determined. Capturing images had to be completed quickly otherwise the film would begin reducing under the electron beam radiation.

2.2.3 Functional Group Determination

2.2.3.1 X-ray Photoelectron Spectroscopy (XPS)

A Kratos AXIS Ultra was used for all XPS measurements, which uses an Al-κα source (1486 eV). The use of the coaxial charge neutralization system was required for all GO samples and the parameters for this tool depended on use and sample properties. Before running high resolution measurements, a charge study was performed on the carbon 1s peak at varying parameters for the charge neutralization system. If differential charging is observed then a new set of parameters are tested until peak shape remains constant. If peaks were suspected to originate from instrumental error, then other peaks with known peak shape would be utilized to either confirm or disconfirm this suspicion. All charging shifts were corrected to the adventitious carbon peak at 284.8 eV.⁶⁴ Peak shape for all GO samples was set to a Gaussian/Lorentzian mix of 65% Gaussian, using the product formula and background was fit via Shirley formula for all C 1s and O 1s spectra.⁶⁵ The background for S 2p spectra was a linear fit. Peak fitting in this section was performed for general carbon bonding types including C-C (284-285.5 eV), C-O (285.5 – 287.5 eV), and C=O (287.5 – 290 eV).⁶⁴ General bonding types for oxygen were also peak fitted: C-O (533-534 eV) and C=0 (531-532 eV).⁶⁴ Peak fitting for the sulfur 2p peak is slightly different because each present sulfur species has both a $p^{3/2}$ and $p^{1/2}$ peak.⁶⁶ The ratio of $p^{3/2}/p^{1/2}$ is assumed to be 2 for all presented sulfur species and the peak shift of the $p^{1/2}$ peak relative to the $p^{3/2}$ peak is varied between 1.0-1.4 eV.⁶⁶ All atomic percentages were determined by using the following equation:64

$$X_A = \frac{(I_A E^{\alpha})/(R_A T(E))}{\sum (I_i E^{\alpha})/(R_i T(E))}$$
 Eq. 1

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Where R_i is the relative sensitivity factor for the measured intensity (I_i) and T(E) is the transmission function for the instrumental operating mode used to measure the intensity (I_i) at kinetic energy E.⁶⁵ The exponent value α is used to make adjustments according to the analyzer being used.⁶⁵ All Ri and T(E) values were gathered from the VAMAS library in CASA.⁶⁵ To test the accuracy of peak components, two techniques were used. Optimization of the peak parameters was done through correlating with other chemical characterization techniques and the second method was performing multivariate statistical analysis through principal component analysis. The multivariate statistical analysis began by maximizing the fits to the residual standard deviation, which was determined through the following equation: ⁶⁴

$$RSD_n = \sqrt{\frac{\sum_{j=n+1}^{c} E_j}{r(c-n)}}$$
 Eq. 2

Where the E_j represents the jth largest eigenvalue, *n* represents the number of principal components used to reproduce the data, *c* is equal to the number of spectra, and *r* is the number of acquisition channels used to construct the data matrix. Using this value, two further statistical terms can be calculated named the IE_n (Imbedded Error) and the IND_n (Indicator Function) given by:⁶⁴

$$IE_n = RSD_n \left(\frac{n}{c}\right)^{1/2}$$
 Eq. 3

And

$$IND_n = \frac{RSD_n}{(n-c)^2}$$
 Eq. 4

These two statistics decrease as the number of primary component fits increase. Once all primary factors are satisfied, the statistics should begin to increase due to interference

from noise in the subspace. Therefore, the minimum can be used as an indicator of the dimensionality of the data subspace and can be used as an estimate for the number of peak components. The final statistic used to help determine the number and fit of components is the chi-squared test, shown here:⁶⁴

$$X_n^2(expected) = (r - n)(c - n)$$
 Eq. 5

This technique compares the expected value and computed X_n^2 value to help determine the number of principal components.⁶⁴ There is a minimum X_n^2 value when the number or principal components is optimized.⁶⁴

Multiple techniques were used to prepare the samples. To analyze powders the material was dried at room temperature because even mild heat (130°C) could cause reduction.¹⁰ Therefore, GO powders were first placed in a desiccator for a minimum of 24hrs. Once powders were de-hydrated a preparation station was created in the XPS room using aluminum foil and a fume hood. Next, a silicon substrate (5x5mm) was prepared by cleaving, cleaning and applying 3M double-side sticky tape. The powder would then be laid out on the aluminum foil and the Si substrate double-side tape surface was then placed on top of the powder and pressed firmly. Using a N₂ blow gun and vacuum, powder that did not stick to the tape was cautiously blown off the Si substrate. This step was repeated until there was a complete film of powder and none of the tape could be seen using a 40x optical microscope. This sample was then ready for measurement.

GO paper material was prepared for XPS in a manner that allowed the material to be used for later studies. The paper was grounded to the XPS sample mount bar using copper plates and a copper clip. These copper clips and plates were mounted down with enough force to cause the GO paper to lie flat, while also electrically grounding the insulating material. This was also prepared in the fume hood to help eliminate dust particulates from agglomerating on the surface.

2.2.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

Infrared (IR) spectroscopy is used to identify chemical species in a material through the absorption of IR light. The IR absorption only occurs for normal modes, Q_i , that change the molecular dipole moment, μ , $(\partial \mu / \partial Q_i) \neq 0.67$ The absorption energy is dependent upon the mass of the atoms, length/strength of the bond as well as the specific vibrational mode: stretch, contract or bend. The intensity of these absorptions is dependent upon the $(\partial \mu / \partial Q_i)$ quantity. And finally, the peak FWHM is determined by intermolecular interaction, most often hydrogen bonding.

A Bruker Hyperion 3000 and Tensor 27 FTIR were used for all IR spectroscopy measurements. Several techniques are available in this system but the three that were used for this project were Germanium Attenuated Total Reflectance (G-ATR), Diamond Attenuated Total Reflectance (D-ATR), transmission, and reflection IR. The G-ATR samples were prepared by spin depositing mono- to few-layer GO onto Si substrates that were 1.5"x1.5". The native oxide of the Ge crystal had to be controlled and found that a mix of organic solvent wipe (isopropanol followed by methyl-ethyl-ketone) and high power UV lamp was the best way to clean any residue left on the Ge from previous runs. After performing the organic solvent/UV lamp cleaning step, the Ge crystal surface was undisturbed for 3min to allow the natural oxide to fully return. Measurements of just the Ge crystal are taken during each step of the cleaning process (prior to and after organic solvent, after UV, and each minute during the oxide growth process). A 'standard' sample of gold deposited on silicon wafer was measured after the oxide growth step. This sample was used after each cleaning procedure and between each GO thin film sample measurement to determine if any particles are transferred to the Ge crystal itself. Measuring the samples required the thin film side to be sandwiched onto the Ge crystal face and a force of 200 N was applied to ensure good contact between the two surfaces. Each measurement had a line resolution of 6 cm⁻¹ and 100 single spectra acquisitions and this resolution was used for all IR measurement types.

The only sample used for the D-ATR was the expanded graphite starting material. This was prepared by covering the diamond substrate with the expanded graphite powder and

applying 200 N of force to ensure a good contact between the powder and the diamond substrate. Because this sample signal to noise ratio was very low the scan resolution for this sample was extended to 400 scans, with a step size of 4 cm⁻¹.

Transmission measurements could only be performed on GO paper and the thickness could not exceed 10 μ m. In order to allow re-use of the paper material the samples were mounted down onto a transmission mounting stand using the back-side of tape. The GO/BCON paper material would only touch the back side of the tape and the extensions of the tape on either side would be secured to the transmission mount using the adhesive side of other tape. The paper was mounted in a way so that part of it was dangling down from the transmission mount and there was no obstruction between the laser source, the paper and the detector.

Reflectance measurements were performed on an IR Hyperion 3000 microscope system. The samples were prepped by either spin or drop casting GO onto silicon substrate. Using the microscope, individual GO flakes varying from $1-5 \ \mu m^2$ could be centered into the beam path and then the IR spectra could be identified for that individual flake.

2.2.3.3 Raman

Raman spectroscopy is a method used to understand the chemistry and defect structure of a material, specifically the ratio of sp² and sp³ hybridization. Each peak in the Raman spectra is a result of phonon excitation induced by a laser source, which in turn promotes the generation of photons with specific energies. Atoms are only Raman active if the polarizability varies as the atoms are displaced collectively along a normal coordinate $((\partial \alpha/\partial Q_i)_0 \neq 0)$, where α is the polarization and Q_i is the normal coordinate or stretch mode. In graphite there are several specific modes that are active and they are presented in Table 6, along with the associated description of what that mode represents. Some of these modes are also present in GO, and further information is provided if variation of these specific peaks occur for the GO material.

Peak/Mode	Position cm ⁻¹	Description
D	~1350	Breathing mode which is activated by sp ³ bonding defect
G	~1580	In plane stretching of C-C bond (sp ² bonding)
D'	~1620	Double resonance in intravalley process (double resonance process)
2D	~2650	Electronic band structure
D+G	~2900	Lattice disorder (5-7-5 or 5-8-5 rings)
D+D'	~2940	Defect present in both the K and Γ direction of the Brillouin
2D'	~3200	Optical wavefunction phonons

Table 6 - Raman peaks for graphite material, their location and what they signify.⁶⁸

In a crystalline structure, such as single crystalline graphite, the source of peak broadening is interaction with other elementary excitations. The elementary excitations that contribute to this full-width-half-maximum (FWHM) broadening are surrounding phonons as well as excited electron-hole pairs. Materials with disorder (exhibit a D peak) will also cause broadening in the G peak. The FWHM of the G peak for single crystalline graphite is ~13 cm⁻¹.⁶⁸

All Raman was performed on a WITec CRM200 using a 488 nm wavelength laser source and both a 40x (NA=0.6) and 100x (NA=0.9) objective, which yielded a lateral resolution of 488 nm and 325 nm respectively. The confocal Raman system was able to capture both 1D and 2D scans of solid samples. Typical resolution for line scans was 2 data pts/µm and the 2D images varied from 2-3 data pts/µm. The integration time for each data point also varied from 1-3 seconds depending on the intensity of the signal. Samples that were measured for total coverage and homogeneity measurements were measured in five arbitrary locations on samples that varied from 1-25 cm². The spectral data could be manipulated using several different algorithms included in the WITec software. The filters used for the GO and graphite data included an assessment of the maximum peak value, integration of peak area, FWHM, and COM for the peaks presented in Table 6. Using the ratio of the D peak integrated area and G peak integrated area (I_D/I_G), the crystallite size (L_a) of the graphite flake can be determined with the following: ⁶⁹

$$L_a(nm) = 2.4 \times 10^{-10} \lambda_L^4 \left(\frac{I_D}{I_G}\right)^{-1}$$
 Eq. 6

Where, λ is the wavelength of the laser source used for Raman. The crystallite size of GO could not be determined from the D and G peaks because there is significant convolution of peak representation within the peak envelope.⁷⁰ However, the D/G ratio of the peak maximum gives a relative relationship of sp3/sp2 bonding in the GO material.⁷⁰

2.2.3.4 X-ray Diffraction Spectroscopy (XRD)

Crystalline phases in materials diffract incident x-rays in accordance with Bragg's law $(\lambda = 2dsin\theta$, where d is spacing between planes and for this instrument $\lambda = 1.542$ Å) which can be used to identify the true identity of the material as well as structural properties.⁷¹

The XRD instrument used for graphite and GO powder structure measurements was a SCINTAG 2 system. This instrument uses a Cu- $\kappa\alpha$ source (1.542 Å) and samples were run with and without a monochromator on the diffracted side. The graphite and GO powder samples were mounted using a zero background holder with a smear mount held at the same orientation for each sample. The scan mode is a step scan measured in 2- θ over a range of angles from 0° to 70°. The step size of the scan is 0.01° with a 0.5 second dwell time at each increment.

2.3 RESULTS

2.3.1 Graphite Powder

Analysis of the starting powder material was first performed so that the relative changes in structure and chemistry during oxidation/cleaning could be identified. As discussed in section 2.1 the graphite materials are natural flake (average diameter of 500 μ m & 50 μ m), expanded flake (300 μ m) and synthetic graphite (5 μ m) and will be referred to as NF500, NF50, EG and SG, respectively. To understand these materials the starting crystallographic structure was determined through XRD, the particle size was measured with both SEM and mesh sieves, the chemical purity and atomic percentages were quantified using XPS and specific bonding structures/defects were assessed through both Raman and FTIR.

2.3.1.1 Structure

X-ray Diffraction (XRD)

The graphite powders measured in XRD were measured with and without a diffraction monochromator installed. Comparisons of these measurements are shown in Appendix A. The monochromator was used to minimize the instrumental lines. The instrumental lines are a result of various x-ray sources from the tungsten filament and copper anode. These x-ray signals are very low and their presence is often only seen for highly crystalline materials. Figure 11 is XRD plots of the starting material scanned without the monochromator, and instrument lines circled.



Figure 11 - XRD scan for all graphite materials without the use of the diffraction monochromator. All graphitic peaks are labeled. The circled peaks are instrumental lines.

Evident in Figure 11, NF500 and EG have limited representation of the expected graphite diffraction peaks. EG exhibits the {001} family of crystal planes and NF500 has a very small presence of the (101), (103) and (110) diffraction planes. This illustrates that during preparation of these graphite materials the powders are most likely stacked in a preferential direction, with the {001} orthogonal to the x-ray beam. The reason for this preferential stacking is likely due to the increased flake size of these materials. It is also expected that the EG material has a slight increase in the interlayer spacing, as determined by shift in the (002) diffraction peak, which would also explain why the other characteristic graphitic diffraction peaks are not present in this scan. A higher resolution scan of the (002) diffraction peak (Figure 12) highlights a shift in the EG material in this direction.



Figure 12 – The shift in the (002) diffraction peak position is highlighted for each graphite material. This peak position represents the interlayer spacing in graphite.

The calculated spacing parameter for each diffraction plane present in the XRD scans are shown in Table 7. It can be seen that the EG material does indeed have the greatest interlayer spacing as well as the greatest c-axis spacing, determined by the position of the (001) peak shown in Figure 12. It is not common for the (001) peak to be present in the XRD scan of graphitic material, but after the diffraction monochromator was used the peak was clearly present. The location of the (001) peak (Table 7) nearly matches the expected distance of the c-axis parameter, 6.71 Å, for the graphitic unit cell.

Table 7- Calculated distance parameter for different crystal planes using the center of mass (COM)from the XRD spectra for each graphite. Results show the spacing is nearly identical for each graphite.

Graphite	Calculated	Calculated	Calculated	Calculated	Calculated	Calculated
material	d(001) [Å]	d(002) [Å]	d(100) [Å]	d(101) [Å]	d(102) [Å]	d(103) [Å]
Natural	6.71 <u>+</u> 0.05	3.36 <u>+</u> 0.03	2.30 <u>+</u> 0.02	2.20 <u>+</u> 0.02	2.00 <u>+</u> 0.02	1.78 <u>+</u> 0.02
(50um)						
Natural	6.70 <u>+</u> 0.05	3.35 <u>+</u> 0.04	-	-	-	1.78 <u>+</u> 0.02
(500um)						
Expanded	6.71 <u>+</u> 0.05	3.38 <u>+</u> 0.03	-	-	-	-
(300um)						
Synthetic	6.70 <u>+</u> 0.05	3.36 <u>+</u> 0.03	2.30 <u>+</u> 0.02	2.20 <u>+</u> 0.02	-	1.78 <u>+</u> 0.02
(5um)						

The c-axis spacing of 6.71 Å translates to a 2-0 value of 13.2°, when using Bragg's law for the Cu-K-beta x-ray source. To determine the exact c-axis spacing for these graphite materials, high resolution XRD scans were performed and it was found that the (001) peak is located near 13.2° for each graphite material, as shown in Figure 13, however the center of mass slightly varied for each as shown by the varying c-axis distance values in Table 7. The (001) c-axis spacing for each graphite material is approx. 6.7 Å and the intensity decreases as a function of particle size. The peak maximum for SG appears at 13.2°, even though the peak is difficult to distinguish. The peak at 8.8° is listed as a potential peak in Appendix A of the tungsten W-L-gamma 3 radiation bypassing the monochromator. However, this is also where the (001) peak shows for the GO material, but it is unlikely that the NF500 graphite material is pre-expanded to 10.9 Å.



Figure 13 - High resolution XRD scan of (001) diffraction peak in each graphite material.

The full width half maximum (FWHM) of the XRD diffraction peak (Table 8) is used to determine the crystallite size of the graphite. The peak FWHM can also be affected by instrumental effects as well as any strain present in the powder material itself. The specific instrumental affect was not investigated, however each material was measured using the same instrument and technique, therefore the values can still be used to compare the relative crystallite size. The peak width (B) is inversely proportional to the crystallite size (L) as shown in the following equation:⁷²

$$B(2\theta) = \frac{K\lambda}{L\cos\theta}$$
 Eq. 7

Where K is a constant of proportionality that varies from 0.62-2.08 and λ is the wavelength of the incident x-ray.⁷² The constant of proportionality, K, is dependent upon many variables including instrumental affects, crystallite size distribution of the material, and crystallite shape. These values are also dependent on the crystallite axis being calculated (a-axis and c-axis). However, assuming that the crystallite orientation/size distribution is similar, and using previously determined K values for other graphite materials (Ka = 1.84 and Kc = 0.89) the crystallite size is calculated and shown in Table 8.⁴⁷

Sample	(002) peak FWHM (Å)	Lc (Å)
NF500	0.26	31.8 <u>+</u> 0.5
SG	0.31	20.9 <u>+</u> 0.8
NF50	0.61	20.2 <u>+</u> 1.0
EG	0.72	5.2 <u>+</u> 1.2

Table 8 - Comparison of the crystallite size for each graphite material

The crystallite size of the graphite material is important to understand because it may be able to affect the ratio of the functional groups present in the oxidized material, which is explored in section 2.3.2.5. These particle flake sizes are further examined by using mesh sieves and scanning electron microscopy (SEM).

Particle Size

To determine the size distribution, each graphite material was weighed after filtering through multiple mesh sieves (Figure 14). Sieves only measure the cut-off value for a particle size, therefore the number of sieves used directly correlates with the resolution of the particle distribution. In the NF500 material it is shown that 78.6% of the material ranges in particle size from 500-850 μ m and 81.4% of the EG material ranges from 300-600 μ m. Because both the NF50 and SG materials are finely ground graphite materials, the range of particle sizes is significantly less and a finer range of mesh sieves are used to determine the distribution. It is clear that the particle range for synthetic graphite is significantly less than any of the other materials.



Figure 14 – Mesh sieves are used to determine the graphite particle size distribution for NF50 (a), NF500 (b), SG (c) and EG (d).

Graphite material morphology and particle flake size was investigated using scanning electron microscope, Figure 15. The micrographs show each graphite material has flake morphology for all samples, but the particle size is drastically different for each. As determined by the mesh sieve analysis, Figure 14, the particle range is quite vast and a significant portion of the NF50 and SG flakes are sub-micron.



Figure 15 - SEM images of synthetic (a), natural - 50um (b) and expanded (c) graphite material, showing similar morphology but on varying scales.

Raman

Each graphite powder material was characterized through multiple survey scans, where Figure 16 shows representative spectra for each graphite material. The primary peaks present in each spectra are the D peak (\sim 1350 cm-1), the G peak (\sim 1560 cm-1), the 2D peak (\sim 2720 cm-1), and the 2D' peak (\sim 3240 cm-1).⁶⁸



Figure 16 - Survey scans in Raman for each graphite material. All peaks of interest are labeled in the first survey scan, but apply to all spectra shown. The ratio between the D and G peak provides information on the crystallite size along the La direction.

As noted in Table 9, there are slight differences in the defect structure for each graphite material. The ratio of the D peak to the G peak (I_D/I_G) signifies the size of the pristine sp²

domain of the graphite structure, L_a . The defect free area is calculated for each graphite material using Equation 6, where the smaller ratio value represents a larger defect free area in the basal plane. The NF materials have the largest sp² domain structure and the larger NF500 has a crystallite size that is 2x greater than the NF50 material.

	Ra	aman	XRD	
	I _D /I _G	<i>L_a</i> (nm)	<i>L_c</i> (nm)	
Natural (500µm)	0.041	332 <u>+</u> 50	31.8 <u>+</u> 0.5	
Natural (50µm)	0.096	142 <u>+</u> 23	20.9 <u>+</u> 0.8	
Expanded	0.235	58 <u>+</u> 47	20.2 <u>+</u> 1.0	
(300µm)				
Synthetic (5µm)	0.112	122 <u>+</u> 45	5.2 <u>+</u> 1.2	

Table 9 - The D/G intensity ratio and the calculated defect free area (L_a) as well as the peak ranges for the peaks of interest in each graphite.

Crystallite size calculation for the a-axis from Raman correlates with the c-axis crystallite axis calculation from the XRD measurements. The two techniques analyze the structure on different scales: Raman can be used to analyze on the micron scale while XRD analyzes the bulk material. In summary, the sp2 domain size is quantified using the Raman spectroscopy technique and the results follow the same trends for the Lc crystallite length determined from XRD for most graphite materials. But most importantly, the size of the crystallite is orders of magnitude smaller than the respective flake size for each graphite material.

2.3.1.2 Chemistry

X-ray Photoelectron Spectroscopy (XPS)

Each graphite starting material is synthesized or mined through different processes, therefore it is expected that the chemistry and purity of the material will vary. Using XPS, the surface chemistry of graphite powder material is investigated. Elemental analysis is performed by scanning all binding energies from 1350-0 eV, shown in Figure 17, and using the atomic concentration calculation shown in the experimental methods for XPS.



Figure 17 - XPS of each graphite material showing slight variation in photoelectron peaks present in the survey spectra.

As shown in Table 10, the EG material has the widest variety of elements present in the surface composition and the lowest carbon purity. The sulfur content of the EG in the XPS survey is also lower than what was presented by the supplier (see Table 4 in section 2.1.1.1). Other elements present in the EG composition are oxygen, sodium and nitrogen. It is often expected for a small amount of oxygen to be present on the surface of most materials, especially if any adventitious carbon is present. Ways to overcome this would require ion etching, but this technique can cause the chemical structure of the material to change and is used sparingly. It is incredibly challenging to differentiate between adventitious carbon and graphite because the peaks are at the same position. The sodium and nitrogen present in the EG material are potentially a result of the intercalation of the bisulfate layer and the cleaning process used by the supplier.

The NF materials have similar carbon purities, with the NF50 sample showing a slightly higher percentage. The only impurity in the NF500 sample is oxygen, while the NF50 sample has very low concentration of sodium, which may have resulted from insufficient ash removal during the cleansing process. Silicon is also present in the survey scan and it is

assumed that this is a result of incomplete coverage of the NF50 powder that is dispersed onto a silicon substrate.

From the XPS survey, it is determined that the SG material has the highest purity, which is expected because of the high temperature synthesis of these petroleum cokes. As mentioned previously in the introduction, this high purity is one reason why these materials are often used for electrochemical applications.

Table 10 - List of the elemental composition for each graphite material as determined by the XPS survey.

	Carbon (%)	Oxygen (%)	Sulphur (%)	Sodium (%)	Nitrogen (%)
Expanded	92.7 <u>+</u> 1.0	6.0 <u>+</u> 1.0	0.6	0.5	0.2
Natural (500um)	93.9 <u>+</u> 1.0	6.1 <u>+</u> 1.0	-	-	-
Natural (50um)	93.1 <u>+</u> 1.0	6.8 <u>+</u> 1.0	-	0.1	-
Synthetic	95.8 <u>+</u> 1.0	4.2 <u>+</u> 1.0	-	-	-

The chemical bonding type and purity of sp² bonding in each material is further investigated by examining the peak shape for the carbon 1s (C1s) photoelectron as well as the oxygen 1s (O1s) photoelectron. Using these two scans, the amount and type of carbonoxygen bonding can be determined. The C1s spectra for each graphite material are compared (Figure 18a) and the peak fitting for each exhibits only two components (Figure 18b), C-C bonding (284.8 eV) and C-O bonding (286 eV). The residual STD (RSD) for this synthetic C 1s component was minimized to a value of 3.4, which also coincided with the minimum value for the X² value of 7.5E-26.



Figure 18 - High resolution XPS scans of the C 1s peak for each graphite material (a) and with peak fitting for the synthetic graphite material (b).

This component analysis for the synthetic graphite material suggests that all the oxygen present in the system is chemisorbed to the graphite, forming this C-O bond. This component peak analysis was performed for the remaining graphite materials and is presented in Table 11. All of the components presented where optimized by finding the minimal RSD and X² values. What this component analysis reveals is that the oxygen in the larger flake materials, NF500 and EG, is primarily bonded to another element or is physisorbed to the surface of the graphite.

T = [1] = 44 $T = [1] = 1$ $(1) = 1$ $(1) = 1$		
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	Natural Flake	Natural Flake	Expanded Flake	Synthetic	
	(50um)	(500um)		Graphite	
C-C (%)	93.8	98.4	98.8	95.7	
C-O (%)	6.2	1.6	1.2	4.3	

The oxygen 1s peak for the EG sample shows that there is clearly more than one peak fit present. When maximizing the fitting arrangement to reduce the RSD & X² value, it is determined that the three peak fitting scheme (Figure 19) is required for the oxygen 1s spectra. The peak at 532.4 eV is found in all the other graphite materials and is representative of C-O bonding. Another oxygen containing species that has the same peak value of 532.4 eV is sulfuric acid (H₂SO₄). It is also possible that during acidification of EG, some of the sulfuric acid is un-reacted and remains in the material. The lower energy peak in the oxygen 1s spectra for the EG sample is assumed to originate from sodium.



Figure 19 - High resolution XPS scan of the oxygen 1s peak for expanded graphite, showing a three component fit representative of C-O (532.6eV) and S-O (531.7eV). The peak at 533.5 eV could be a result of water.

As mentioned previously, one explanation for the presence of sodium in the survey scan is the formation of a sodium bisulfate (NaHSO₄) or sodium sulfate (Na₂SO₄) during the acidification of the EG material. Using the NIST Database of XPS spectra for chemical species, it was determined that the sodium bisulfate, sodium sulfate and sulfuric acid have an oxygen 1s peak present in the range from 531.5-535.2 eV.^{73,74,66} The other elements for these chemical species (Na₂SO₄, NaHSO₄, and H₂SO₄) are also listed in Table 12 and compared against the empirical measurements of the EG material.

	P	Reference		
	Sulphur-2p ^{3/2}			
EG (measured)	168.7/169.8/171.1	531.4/532.4/533.5	1071.3	-
Na ₂ SO ₄	167.5-169.2	531.1-532.1	1071.2-1072.5	74
NaHSO ₄	169.3-169.5	532.3/533.6	1071.6	66
H ₂ SO ₄	169.3-169.9	532.4/533.9	-	73, 66

Table 12 - Comparison of peak positions for elements present in expanded graphite material andsuspected chemical species present in the graphite

These results indicate that the presence of excess oxygen in the EG sample is primarily a result of one of these sulfur species. The best explanation for the excess oxygen in the NG500 samples is oxygen physisorbed to the surface of the graphite material.

XPS reveals that NF50 exhibits the highest percentage of C-O bonding, which could affect the subsequent sp2 domain size and C/O ratio in the oxidized material. It was also determined that SG has no other constituents other than carbon and oxygen. Lastly, NF500 and EG exhibit the lowest quantity of C-O bonding and the excess oxygen in EG most likely originates from sulfur compounds.

FTIR

The dipole moment change for crystalline graphite is very small under IR activation, therefore the only sample that was measured with this technique was the EG sample. It was measured using the Diamond-ATR system. A baseline correction was performed to assist in the identification of present peaks in the spectra and the original spectra can be found in Appendix B.



Figure 20 - D-ATR of EG powder with labeled peaks. The noise from 1700-2300 cm⁻¹ is characteristic of water vapor and CO₂ being present on the surface of the material.

Infrared data suggests that both the bisulfate ion HSO⁴ and sulphuric acid may be present in the EG structure and that there is limited intermolecular interaction between the EG layers. There could also be intercalated water in the EG structure as shown by the presence of all the OH normal modes. The XPS results for EG did show a small presence of both C-O bonding and elemental sodium matching the peak location for sodium bisulfate, therefore the IR spectra shown in Figure 20 confirms that either one or both of these species are present in the graphite.

The peaks shown in Figure 20 at 3450 cm⁻¹, 1600 cm⁻¹ and 665 cm⁻¹ are all characteristic of OH stretching, scissoring and bending, respectively. Bisulfate (HSO₄⁻) and sulphuric acid (H₂SO₄) have similar peaks present in the range of 1190-1160 cm⁻¹, 1080-1000 cm⁻¹, 880-840 cm⁻¹ and the spectra shows a peak within each of these ranges at 1185 cm⁻¹, 1060 cm⁻¹ and 870 cm⁻¹. The peak at 870 cm⁻¹ is likely the S-OH stretch peak for HSO₄⁻ (which is in agreement with XPS results) and it is possible that the FWHM is small because there is limited intermolecular interaction between the layers of EG, therefore providing minimal resistance to this vibration mode. The peak at 1225 cm⁻¹ could either represent a C-O-C asymmetric stretch or asymmetric stretching of SO2 in the sodium bisulfate (NaHSO₄⁻).

The other strong peak from the sodium bisulfate species occurs between 700-570 cm⁻¹, and this range overlaps with the OH bending peak. The peak at 2344 cm⁻¹ is most likely the result of noise from the water and CO₂ vapor, because the only species that show up in this range are species with $C \equiv N$ bonding.

2.3.2 GO synthesis effects

2.3.2.1 GO runs

Using the four starting graphite materials (NF50, NF500, SG, and EG), GO was synthesized using both the Hummers method⁴² (now referred to as GOH) and the Tour method⁹ (now referred to as GOT), except the NF500 material, which was only synthesized successfully using the Tour method⁹. The following Table 13 lists all the materials synthesized, the measured temperatures during important steps, time of oxidation, and the percentage of H_2O_2 added at the final step.

For the remainder of this thesis, specific GO synthesized material will be referenced by the run number, ex. GO4. Before discussing the results for these runs it should be pointed out that GO runs 7, 13, and 15 were not characterized due to unsuccessful oxidation. An explanation why these runs failed can be found in Appendix C. The remaining successful runs will be discussed in the following sections and Table 13 can be used as a reference tool.

GO	Method	Graphite	Graphite	Temp	Stir	Stir	Stir	Quench	%H ₂ O ₂
run	(Hummers -	Material	mass (g)	powder	time	Temp	rpm	Temp	
#	H, Tour - T)			(°C)	(min)	(°C)		(°C)	
4	Н	SG	20.0	19.0	120.0	30.0	600.0	91.3	17.4
5	Н	NF	3.0	17.0	120.0	35.0	200.0	60.0	0.2
		(50µm)							
6	Т	NF	3.0	43.0	120.0	50.0	200.0	70.0	0.1
		(500µm)							
8	Т	NF	3.0	38.0	2640.0	36.0	200.0	60.0	0.1
		(500µm)							
9	Т	SG	3.0	44.0	1000.0	53.0	300.0	70.0	0.1
10	Т	EG	1.5	41.0	850.0	52.0	200.0	42.0	0.1
11	Н	EG	3.0	19.0	120.0	40.0	200.0	101.4	0.2
12	Т	NF	1.5	42.0	480.0	58.0	200.0	55.0	0.1
		(50µm)							
14	Т	NF	3.0	41.0	720.0	50.0	200.0	63.0	0.1
		(50µm)							
16	Т	NF	9.0	44.0	700.0	50.0	200.0	50.0	0.1
		(50µm)							

Table 13 - All oxidation runs are shown in this table highlighting important parameters for the synthesis process. All GO material will be referenced to by the run number. For example GO4 is a reference to the GO material synthesized during run number 4.

2.3.2.2 Oxygen presence and (001) d-spacing

Using multiple high resolution XPS measurements for each GO material the mean C/O ratio was determined as well as the standard deviation (Figure 21a). Values were determined through integration of the oxygen 1s and carbon 1s peak, where no peak fitting was performed. Therefore ratios include any water content present within each structure. To
determine the exact amount of oxidized carbon, peak fitting of the carbon 1s spectra was subsequently completed for each GO run (Figure 21b).



Figure 21 - XPS of each GO material was used to determine the C/O ratio (a). To determine the accuracy of each measurement, multiple tests were run on each sample and the error bars show the C/O deviation. The % oxidized carbon was determined through peak fitting analysis for each carbon 1s spectra (b). The difference between these two evaluations is that the C/O ratio includes water content and the % oxidized carbon excludes the water content.

Both evaluations are useful because both water and the oxidized carbon play a role in the structure and chemistry of GO. GOT samples (runs 6, 8, 9, 10, 12, 14 and 16) for all starting graphite materials have a lower C/O mean than GOH from the equivalent starting graphite material (runs 4, 5, 11). The only material with a C/O greater than 2 is the EG oxidized sample, GO11, which is not typical for GO synthesis as mentioned in the introduction (see Table 3). However, the percentage range for the oxidized carbon, 55.8 – 71.1 %, is closer to what is seen in the literature (see Table 3). The discrepancy is an indication that there is intercalated water present in most structures, especially GO4 and GO6.

To understand if oxygen fraction translates to an increased separation between layers of GO, XRD analysis is performed. The change in the interlayer separation is measured relative to the parent graphite separation. Because these materials have been oxidized, the (002) peak is diminished and the primary peak in the XRD spectra is the (001) peak, which is representative of the layer spacing in the oxidized material. The full XRD scan for each material is in Appendix D, with the high resolution scan of the (001) peak in Figure 22.



Figure 22 - XRD of the (001) peak is compared for SG (a), NG50 (b), and EG (c) and the darker shaded materials are GOT and the lighter shaded materials are GOH.

The (001) diffraction peak for the GOT samples in Figure 22 are all at lower 2- θ values relative to the GOH samples of the same starting graphite material, which represents a greater inter-layer spacing. The separation of the peak center between G05 and G012 is not as significant as the other GO materials, which correlates with the oxygen content calculations for these materials. Further discussion on this interlayer relationship will be discussed in following sections, specifically investigating oxidation processes, cleaning effects and parent graphite characteristics. Both GO4 and GO11 have a shoulder peak on the higher $2-\theta$ side at 12.5° and 11.4° , respectively. This could possibly be related to incomplete oxidation of the graphite material. This hypothesis is re-enforced by the presence of the (002) peak in the G011 structure, shown in Appendix D. The reason the GO11 & GO4 (001) peak does not show up at the same location of the graphitic material (13.1°) may be due to oxidation of graphite edges, but incomplete oxidization of the basal plane, which has been reported previously for lightly oxidized GO material.⁵⁴ This affect would lead to an average separation value between completely oxidized GO (>8 Å) and pristine graphite (3.45 Å). The interlayer spacing is calculated from the (001) diffraction peak position for GO materials shown in Figure 22 and the increase in the interlayer spacing is compared to the (002) diffraction peak position for each respective parent graphite material, as shown in Table 14.

Table 14 - Analysis of the (001) diffraction peak center of mass and the relative shift after oxidation of each parent graphite material shows the total increase of the inter-layer spacing along the c-axis of each oxidized material.

	Δd(001) =	Δd(001) =		
	GOH d(001) - Graphite d(002) [Å]	GOT d(001) - Graphite d(002) [Å]		
Natural - 50	5.48	5.53		
Expanded	4.76	5.99		
Synthetic	5.23	5.31		
Natural –	_	8.18		
500				

The sample with the greatest increase in the c-axis direction after oxidation occurs for the GO6 sample, NF-500 parent material, with a final interlayer separation of 11.53 Å. The greatest variation in interlayer spacing between oxidation methods for specific starting graphite occurs for the EG material (GO10 and GO11), a difference of 1.23 Å. Because the temperature for both GO10 and GO11 does not reach 180°C, it is assumed that the effect of expansion cannot be a result of bisulfate expansion.⁵⁷ Figure 23 summarizes the data shown in this section.



Figure 23 - Diagram depicts the correlation between the oxygen content and the c-axis spacing for each measured GO run. The trends for each GO run are shown in each arrow. The parameters of each GO run can be found in Table 13, but the legend to the right specifically highlights graphite material was used for the respective GO run.

The connections shown in Figure 23 highlight two parameters that affect the c-axis spacing: starting material and level of oxidation. The diagram shows distinct pairing of GO with the same parent material, specifically for the SG (GO4 & GO9) and the NF50 (GO5 & GO12) oxidized samples. Even though samples GO4 & GO9 have higher oxygen content than the GO5 & GO12, their interlayer spacing is smaller. This indicates that the starting material may have an impact on the separation of layers during oxidation. The interlayer spacing may be affected by three different parameters of the starting material: flake size, flake morphology and starting chemistry. These parameters are further investigated in the following sections.

Within each set of samples from the same parent graphite material, the GO with greater % oxidized carbon (excluding water) is always the material with greater interlayer spacing. This is a direct contradiction with Shao et. al.,⁵⁴ who determined interlayer spacing did not increase as a function of oxidation. This conclusion is also supported by the full XRD scans

shown in Appendix A for each GO material. The GO runs 4, 9 and 11 all have graphitic peaks present in the full XRD scan, which indicated incomplete oxidation. The percentage of these graphitic peaks in the full XRD scan for each material are 10.3%, 9.6%, and 0.8% for GO runs 11, 4, and 9 respectively. The total interlayer spacing increases as the percentage of graphitic peaks decrease between each of these runs as seen in Table 14. It is also possible that varying parameters during the oxidation and cleaning procedures could affect the interlayer spacing and oxidation. The following section explores the source of ordering shown in Figure 23, specifically focusing on highlighted parameters in Table 13, cleaning procedures, and starting material characteristics.

2.3.2.3 Oxidation Process Effect on GO

There is a direct correlation between the temperature of the suspension during the addition of water and the interlayer spacing (Figure 24), excluding GO-6. The reason GO6 does not match this trend is likely related to the parent material and will be discussed in section 2.3.2.5. GO4 and GO11 were not cooled to room temperature before being added to the water/H2O2 solution, because these samples were run through the Hummers process. Only GO5 was cooled prior to adding it to water and the maximum temperature reached 60°C. It is probable that even though GO5 is a GOH material, cooling the acid slurry before water addition promoted greater interlayer spacing, which is nearly equal to the GOT from the same parent graphite, GO12. As mentioned in the introduction, cooling the acid slurry before water addition can yield an increase in the oxygen level and c-axis spacing.^{16,55} The c-spacing and T-water values for GO5 & GO12 helps confirm that this processing step may be the key difference between Tour method and Hummers method. However, other factors affect the interlayer spacing may be the specific starting material used or the cleaning process, due to the GO6 anomaly shown in Figure 25. Additionally, the oxygen level of the GO runs do not correlate directly with the temperature during the water addition indicating other contributing factor to the overall oxygen content of each material.



Figure 24 - Diagram compares the c-axis spacing of each GO run to the maximum temperature reached during the addition of water in the final step of the oxidation. Specific parameters for each GO run can be found in Table 13. The trends here show that as the quenching temperature decreases the c-axis spacing increases.

The final significant oxidation parameter variation between the GOH and GOT samples is the mixing temperature/time of the acid slurry. Excluding GO8, the mixing temperatures for the GOH runs are lower than all the GOT samples, which have been cited to lead to lower oxygen content, specifically carboxylic acid, in the subsequent GO material.⁵⁴ The variation in the oxygen content for each GO run is shown in Figure 25b, now highlighting the composition of single bonded oxidized carbon and double bonded oxidized carbon. This composition is compared against the acid mixing parameters shown in Figure 25a. The mean C=O composition, which includes carboxylic acid and carbonyl groups, varies only 6% for all the GO runs and the GOH sample with the highest stirring temperature (GO11) has the lowest C=O value. This is contrary to what was proposed by Shao et. al.,⁵⁴ and suggests that the exothermic reaction during the water addition is more influential over the GO chemistry than the mixing temperature of the acid slurry. However, one factor that may impact the GO chemistry is the mixing time.



Figure 25 – The diagram (a) shows the total acid mixing time and mixing temperature during the synthesis for each GO run and specific values can be found in Table 13. The composition of species present in each GO run is determined through high resolution XPS scan of the carbon 1s spectra (b). The C-O bonding includes hydroxyl (-C-OH), ether (-C-O-C-) and/or epoxide (-C-O) functional groups and the C=O bonding includes carbonyl (-C=O) and/or carboxylic acid (O=C-OH) groups.

All samples that were mixed for at least 700 minutes (marked with dashed line in Figure 25a) have <35% un-oxidized carbon present in the structure and this includes each parent graphite material. However, the sample with the least amount of un-oxidized carbon, GO16 (mean = 28.9%), was oxidized to the 700 minute threshold. Additionally samples GO14 and GO16 were both NF50 materials and had nearly identical oxidation parameters, yet GO14 was slightly less oxidized (un-oxidized carbon mean = 33.8%). The only significant difference during the oxidation process between GO14 and GO16 was the temperature increase during water addition, which has no significant impact on the oxygen content as previously determined. It is possible that this variation is a result in XPS peak fitting error, because the values are not statistically significant. Secondly it is plausible that the cleaning procedures are the source for the oxygen content variation. One final reason why these samples may differ in oxidized carbon is a result of GO meta-stability, which is discussed in Chapter 3.

2.3.2.4 Cleaning Effect

The chemistry of one sample, GO16, was characterized as a function of the centrifuge cleaning process. The sample was first measured immediately after finishing the acid slurry mixing step (before the addition of water). Then the sample was measured after the second round of HCl, ethanol, and water cleansing. Finally GO16 was measured after varying pH values of the water rinsing process. The results from XPS measurements are shown in Figure 26.



Figure 26 - XPS results are compared for a GO material as it progresses through the cleaning procedure. A comparison of the elemental composition (a) and the chemically bonded species to carbon (b) are shown.

Two trends that result from the cleaning process are a decrease in impurities and an increase in oxidized carbon. The sulfur species remaining in the GO structure immediately after the oxidation process has been proposed to be a combination of un-reacted sulfuric acid as well as covalent sulfates.¹⁶ It is likely that the phosphorous material is un-reacted phosphoric acid from the oxidation process. After cleaning the GO material in HCl, ethanol, and water the phosphorous levels drop to approx. 0% and sulfur decreases by 1.3%. These results reconfirm that the phosphorous is not covalently bond and is instead residual acid from the oxidation. Another key observation from Figure 26 is that the overall oxygen

increases 2.5% and the oxidized carbon increases 13% after the cleaning process is complete. This change in oxidized carbon is discussed later.

After continuous water rinsing (up to 1,500 ml of water per gram of material) the pH level of GO16 increases to 3 and the sulfur content decreases until it reaches a steady state value of \sim 0.4%. The use of both XPS and FTIR help to show that at least one sulfur species found in EG is the same sulfur species found in the final GO16 material, as shown in Figure 27.



Figure 27 - The remaining sulfur species in GO16 after the cleaning procedure is compared to the sulfur species in EG using both XPS (a) and FT-IR (b). The peak fits in the sulfur XPS spectra include both the 2p3/2 (solid gray lines)) and 2p1/2 (dashed gray lines) for each sulfur species. The dashed lines are representative of either sulfuric acid or a bisulfate ion.

There is no sodium found in the final GO16 material, therefore the only possible sulfur species in GO16 would contain some combination of hydrogen, carbon, and/or oxygen. Therefore the sulfur 2p peak component at 168.7 eV should be a sulfur species containing hydrogen, carbon, and/or oxygen. The FT-IR comparison, Figure 27b, highlights 3 peaks related to sulfuric acid and/or the bisulfate ion (HSO₄⁻) vibrational frequencies that show up in both GO16 and EG. Therefore, it is assumed that this peak at 168.7 eV is related to sulfuric acid or a bisulfate ion. This cannot be re-confirmed using the oxygen 1s peak in XPS because these sulfur species contribute a maximum of 2% of the oxygen 1s peak area for GO16.

	Sulfur 2p ^{3/2} peak position (eV)	Oxygen 1s peak position (eV)			
EG (measured)	168.7/169.8/171.1	531.4/532.4/533.5			
GO16 (measured)	167.7/168.7	531.9/532.7			

Table 15 - list of peak positions from XPS measurements for EG and GO16 (after cleaning process)

The sulfur 2p peak component at the lower binding energy for GO16 could be related to several different sulfur species and the data from FT-IR is too convoluted to determine exactly which species is present in GO16. The following Table 16 lists some of the potential sulfur species with a binding energy of 167.7 ± 1 eV and vibrational frequencies that match those found in FT-IR. The sulfuric acid and bisulfate ion are labeled in this table as a reference to see what organic sulfur compounds overlap in vibrational frequency. If the positions of these organic sulfur compounds are compared with the FT-IR spectra for GO16 in Figure 27b, it can be seen that any variety of the compounds could be present in the GO structure. However, the composition of sulfur in the GO16 sample is ~0.4%, therefore the predominant IR species seen in Figure 27b are likely oxidized carbon compounds. Therefore, the additional sulfur species in GO at 167.7 eV will just be referred to as the organic sulfur compound.





The presence of this organic sulfur compound causes the sulfur 2p peak position to shift to a lower binding energy and signifies a change in the sulfur species. The initial center of mass for the entire sulfur peak after acid slurry removal is 168.8 eV and after the cleaning process this peak shifts to 168.2 eV. This shift signifies a decrease in the sulfuric acid/bisulfate composition and the presence of this organic sulfur species. After multiple water rinses, the sulfur 2p peak position shifts back to 168.6 eV, which is the peak shown in Figure 27a. This shift up in binding energy may be the formation of more sulfuric acid as a result of organic sulfur hydrolysis. Sulfuric acid formation from hydrolyzed organic sulfur was theorized by Tour et. al.,¹⁶ and the hydrolysis is stated to be initiated by the addition of water during the cleaning period, as shown in Figure 7.

The mechanism proposed by Tour et. al., ¹⁶ determined that a second by-product from organic sulfur hydrolysis was the formation of additional oxidized carbon. This helps explain why the oxidized carbon composition increased after the cleaning process (HCl, ethanol, water) was completed. The total amount of water that was used during the cleaning process was 500 ml per gram of parent graphite material and the process lasted longer than two days. The half-life of the hydrolysis interaction is reported to be approximately 15 hours.¹⁶ The expected rate of organic sulfur hydrolysis and the measured rate of oxidized carbon formation is shown in Figure 28 as a function of the amount of time GO is in water. After the cleaning process is complete the amount of oxidized carbon increases a trivial amount and the explanation for this is related to decay in the hydrolysis reaction rate. After extensive washing, approximately 10% of the originally formed organic sulfur compound remains in the GO structure, which contributes to 0.2% of the total composition. It is possible that further cleaning of the GO in a basic solution could remove the remaining organic sulfur compound, but it was not deemed necessary.



Figure 28 - The graph shows the correlation between the change in unoxidized carbon and the amount of time the GO was in water after the oxidation process was completed. Hydrolysis of organic sulfur compounds found in GO occurs in water and induces further oxidation.

In conclusion, it has been determined that the cleaning process significantly increases the amount of oxidized carbon and is most likely the result of the proposed hydrolysis mechanism. The cleaning process also removes a significant portion, if not all, of impurities from the oxidation process.

2.3.2.5 Parent Material Effect

Each graphite material used for GO synthesis has unique characteristics, specifically the crystallite size, flake size, chemistry, and morphology. These characteristics were all explored in section 2.3.1. The effect these materials have on the final GO flake size, thickness and morphology is determined through the use of AFM as well as SEM. The defect free area in GO is also compared to the crystallite size (both La and Lc) of the parent graphite material to determine if it can affect the final size of the defect free area. And lastly, the chemistry and electronic structure of GO is compared to the physical dimensions of the flake and defect free area.

It was found that when a GO suspension in water was drop casted onto a substrate the flakes agglomerate, therefore spin casting was required to study individual flakes. However, even spin casting some samples still resulted in agglomeration, specifically GO10 and GO11. This agglomeration in GO10 and GO11 may have also been a result of large flake size. Figure 29 shows AFM for GO10 and GO11.



Figure 29 - AFM images for GO 11 (a) and GO10 (b) show flakes that extend beyond the scan window, which is $10x10 \mu m$, and significant agglomeration. The images show multiple layers of stacked GO with particle sizes varying from sub-micron to >10 μm .

Samples GO10 and GO11 in Figure 29 are both from the EG parent material. There is significant folding and wrinkling present in both materials in Figure 30, which is likely a result of the large flakes agglomerating during the drying process of the GO suspension. The lines that are present in Figure 30a are representative of the wrinkling effect. Because of the overlap it is difficult to measure the exact size of each flake, but it can be seen that some of the flakes in Figure 29b are folded multiple times and extend outside of the scan. The lower amount of oxidized carbon and decreased interlayer spacing of GO11 relative to GO10 may be the reason why the flakes in GO11 seem to agglomerate significantly more than GO10. Using multiple AFM scans and SEM images (Appendix F) of these oxidized EG materials, a distribution of particle sizes was determined. Nearly 80% of the GO material in



Figure 30c is less than 5 μ m², which is significantly smaller than the average EG particle diameter, of ~300 μ m.

Figure 30 - Histogram of measured particle area from multiple AFM and SEM images for oxidized SG (a) oxidized NF50 (b), oxidized EG (c), and oxidized NF500 (d).

The measured particle area for all the GO materials (Figure 30) indicates that the highest percentage of particle varies from 0-2 um², 100% for oxidized SG (Figure 30a), 82% for oxidized NF50 (Figure 30b), 67% for oxidized EG (Figure 30c), and 39% for oxidized NF500. Even though the starting flake size for each of these materials are vastly different, the ending GO flake sizes are roughly the same. There is just a small increase in the particle size range and this range increases relative to the starting parent material flake size. The SG material particle size was nearly all sub-micron as seen from the AFM images for GO4 and GO9 (Figure 31). The oxidized NF50 material also has a very high percentage of sub-

micron particles, 73%, and this distribution of particles can also be seen in the AFM image for both GO5 and GO12, shown in Figure 32.



Figure 31 - AFM images of GO4 (a) and GO9 (b) including a section scan of the height profile for GO4. The section scan is taken along the dashed line. Both images are set to the same height scale bar.

The AFM scans in Figure 31 also highlight the presence of small flake size that appears as spots. The section scan in Figure 31a further highlights the presence of the small flakes, which show up as noise. The monolayer GO flake thickness determined from the section scan is 1.3nm. The NF500 oxidized material in Figure 33 shows more GO stacking as well as a measurement of an individual flake with a thickness of 1.2 nm. The AFM scan of the GO thin film (Figure 33b) also highlights the agglomeration of the material. The thickness of this thin film could be controlled and the control in thickness variation is highlighted in Appendix G.



Figure 32 - AFM images of GO5 (a) and GO12 (b) including a section scan of the height profile for GO5. The section scan is taken along the dashed line. Both images are set to the same height scale bar.

The dispersion of GO5 flakes was sparse enough to make measurements of the flake thickness and the section scan shows that the thickness is 1.2 nm. This value is close to those reported in literature for single layer of GO.^{54,75} The AFM images for GO5 and GO12 also show less folding and wrinkling than the EG material, which is most likely a result of the smaller particle size. The smaller oxidized SG material also shows no folding or wrinkling, as seen in Figure 31.



Figure 33 - AFM images of GO6 with section scan of the height profile (a) and of a thin film of GO6 (b). The section scan is taken along the dashed line.

Using Raman, the D/G ratio is compared for each GO material which roughly translates to the total defect free area. However, there is no exact empirical formula for the calculation of the defect free area for GO due to the complex nature of all the oxygen functional groups present. ^{76,70} The material with overall lowest mean D/G ratio is GO10 and the material with the highest mean D/G ratio is GO9. It is possible for these materials to have the same total % oxidized carbon yet have varying amounts of specific oxidized carbon structures and/or defects. These oxidized carbon and/or defect species can be identified with Raman, but it requires very accurate peak fitting because there are a variety of possible peaks that could be represented by the broad D and G peaks shown in Figure 34.^{76,70}

Table 17 - The D/G ratio from multiple Raman scans for each GO material is compared.

	G04	G05	G06	G08	G09	GO10	G011	G012
D/G	0.81 <u>+</u> 0.03	0.82 <u>+</u> 0.03	0.77 <u>+</u> 0.04	0.74 <u>+</u> 0.03	0.83 <u>+</u> 0.07	0.72 <u>+</u> 0.01	0.76 <u>+</u> 0.06	0.78 <u>+</u> 0.03

The G peaks for all the GO samples are shifted relative to the parent graphite material and Figure 34 highlights this shift for GO9. The blue shift in the G peak from graphite to GO could be a result of monolayer effects, activation of the D' peak, and/or specific structural motifs related to oxidized carbon or defects. ⁷⁶



Figure 34 - The D and G peak for GO9 (top curve) are compared to the SG parent material G peak (bottom curve). The COM for the GO9 G peak is 1604 cm⁻¹ and the COM for the graphite G peak is 1575 cm⁻¹.

To determine if there was a difference in the oxidized carbon structure between GO9 and GO10, FT-IR measurements were employed. This FT-IR comparison in Figure 35 permitted a qualitative analysis of the oxygen species present in the structure. The detail given by the FTIR measurements show that the variance in peak position between GO9 and GO10 is trivial, but the relative peak intensity varies between the peak at 1741 cm⁻¹ and the peak at 1624 cm⁻¹, which are representative of carboxyl groups (C=O) and aromatic C-C stretching. This variation correlates with an increase in the C=O percentage in GO10, as determined by XPS (Figure 25a), when compared to GO9. Therefore, GO9 and GO10 have the same type of functional groups and a nearly identical overall percentage of oxidized carbon but there is a slight difference in the amount of carbonyl groups, as determined in both XPS (Figure 25a) and FTIR (Figure 35). Previous structural models have shown that the carbonyl groups are primarily positioned along the edge of the GO flake.³¹ Hence, there is likely a greater abundance of functional groups in the basal plane of GO9 than GO10. This increased

confinement of sp³ bonded species could explain why the D/G ratio is higher for GO9 than GO10, because the D/G ratio is a characteristic of the defect free area.⁷⁷



Figure 35 - FTIR images for GO10 and GO9 are shown highlighting the matching IR peaks between samples. Each spectra is normalized so that a qualitative comparison of the peak positions can be made.

The only significant processing variations between GO9 and GO10 are the starting parent materials and the maximum temperature during the addition of water. It has previously been shown in this work that the maximum temperature of the suspension during the addition of water has no correlation with the total percentage of oxidized carbon or the percentage of individual oxygen species. Therefore, the increase of in-plane C-O bonding species for GO9 is most likely a result of the parent graphite material used.

There are three significant differences between the parent material for GO9 (SG) and GO10 (EG). Firstly, the EG material is pre-expanded by an intercalated bisulfate species and the SG material has no impurity other than C-O bonding. The starting C-O bonding in SG is

4.3% and is 1.2% for EG, shown in Table 11. Therefore the chemistry of each material is significantly different. Secondly, the crystallite size of EG is smaller in both the a-axis and c-axis (La = 58 Å, Lc = 5 Å) than the SG material (La = 122 Å, Lc = 21 Å), shown in Table 9. And lastly, the starting flake size is much larger for EG (83%wt range from 300-600 μ m) than SG (89%wt range from 3-45 μ m). Not enough detail is available from the FT-IR, Raman, and XPS analysis of GO9 and GO10 to determine exactly which of these characteristics of the parent material cause this change in chemical structure to occur. However, GO6 and GO12 are both GOT materials synthesized from natural flake graphite, NF500 and NF50 respectively. Therefore it is assumed that the slight variation in C-O bonding between these two materials, 6% for NF50 and 2% for NF500, can be neglected. The NF50 crystallite size (La = 142 Å, Lc = 21 Å) is nearly half the size of the NF500 crystallite size (La = 332 Å, Lc = 32 Å). Also the flake diameter of NF50 (88%wt range from 0-75 μ m) is roughly 10% of the NF500 flake diameter (79%wt range from 500-850 μ m).

Figure 36 is a comparison of FT-IR measurements for GO5, GO6, GO8 and GO12. The reason GO5 is shown in Figure 36 is to demonstrate that the vibrational peaks are nearly a perfect match with GO12, although the NF50 material for GO5 was synthesized using the Hummers method. GO8 is also presented in Figure 36 to highlight that the same parent material, synthesized through nearly an identical oxidation process, and cleaned following the same procedure, yields a drastically different IR spectrum than GO6. It is also important to note that all of these measured samples had <0.5% sulfur composition, as determined by XPS, therefore it is expected that vibrational peak contribution from sulfur species is negligible.



Wavenumber (cm⁻¹)

Figure 36 - FTIR analysis of GO5, GO6, GO8, and GO12 highlights similarities and differences in the present vibrational peaks for each spectra. Both GO5 and GO12 are synthesized from NF50, but GO5 is GOT and GO12 is GOH. Both GO6 and GO8 are synthesized from NF500 and are both GOH materials. Prominent peaks occur at 1741-1750 cm⁻¹ (carbonyl stretch), 1624 cm⁻¹ (water bending), 1415-1440 cm⁻¹ (hydroxyl O-H deformation), 1220-1224 cm⁻¹ (epoxide stretch), 1130-1170 cm⁻¹ (hydroxyl C-O stretch), and 1048-1080 cm⁻¹ (alkoxy stretch).

It is difficult to determine exactly which chemical species is present in each spectra, but it is obvious that the intensity of the peaks ranging from 1000-1130 cm⁻¹ are greater than the peak intensities >1300 cm⁻¹ for samples GO6 and GO8. The vibrational peaks in the 1000-1300 cm⁻¹ range are all representative of C-O stretching, but this C-O stretching could be a result of esters, carboxylic acids, anhydrides, alkoxy, hydroxyls, or ethers.³⁷ The strongest peak for GO6 (1080 cm⁻¹) is likely representative of an alkoxy and the strongest intensity peak for GO8 (1130 cm⁻¹) is likely the result of present hydroxyl groups.³⁷ The peak at ~1750 cm⁻¹ is characteristic of the C=O vibration peak for several carbonyl groups, including carboxylic acid.³⁷ Therefore the analysis from FTIR shows that the C-O species

have a greater presence in GO6 and GO8 than in the GO12 and GO5 samples relative to the C=O species. A greater concentration of C-O bonding in GO6 and GO8 compared to GO5 and GO12 is also confirmed through XPS analysis shown in Figure 25.

The reason for this increased C-O presence in the GO6 and GO8 material relative to GO5 and GO12 is most likely related to the crystallite size of the parent material. The crystallite edges of the graphite material likely act as a nucleation site for the oxidation process and eventually lead to the formation of holes or break the flake off completely to form an individual GO flake. Edges and holes are the location of C=O bonding, such as carboxylic acid. ³⁴ Figure 30 demonstrates that the subsequent range of GO flakes for the NF50 starting material (GO5 and GO12) is 1/50th the GO flake size for NF500 and Table 9 indicates that the crystallite size of NF50 (La =142, Lc =20) is smaller than the crystallite size of NF500 (La =332, Lc = 32). This may explain why the GO5 and GO12 materials have a slightly greater intensity of C=O vibrational peaks relative to the C-O. If the nucleation of oxidized carbon does occur along the crystallite boundary it could also explain why at least 50% of all measured GO flakes for each material are < 3 μ m², even though the starting graphite material flake sizes are drastically different.

2.4 DISCUSSIONS & CONCLUSIONS

Analysis of data shows that a few processing steps have proven to dictate the subsequent GO characteristics. Water plays a key role during the oxidation process, specifically during the mixture of water into acid slurry. Minimizing this exothermic reaction during the mixture of the water and acid results in an increase in the c-axis spacing, which may reduce the sonication energy required to separate individual sheets of GO. Additionally, mixing the graphite in the acid slurry, during the oxidation process, for greater than 700 minutes near the maximum allowable temperature marginally increased the percent of oxidized carbon relative to those materials that were mixed for less time.

The cleaning process was also studied and it was found that water can increase the amount of oxidized carbon in the GO structure. The route for oxidation from hydrolysis of covalent sulfates by addition of water was first proposed by Dimiev et. al.¹⁶ The work presented in this thesis has shown the change in chemistry during individual steps of the cleaning process as a result of this process and the rate of oxidation matches the proposed rate of hydrolysis. The only discrepancy is that a marginal amount of the covalent sulfur species (<0.5%) remains in the GO structure, even after excessive water rinsing.

Lastly, it is proposed in this work that the crystallite size of the graphite material is the most significant quality of the starting material for GO synthesis. Graphite materials with drastically different chemistries were tested and when oxidized under similar conditions and cleaned with identical processes, the final chemistry of the GO was nearly identical. Graphite with larger particle size can yield larger monolayer flakes, but the GO flake size is dramatically reduced in comparison with the starting particle size. It is possible that nucleation of oxidized carbon occurs along the crystallite edge of the graphite. The oxidized edges can reduce the fracture strength of the GO material, therefore this may act as shear location in the (001) plane during mild sonication.³ More work is required to determine if this oxidation along crystallite edges is the sight of initial oxidation.

CHAPTER 3 – GRAPHENE OXIDE RADIOLYSIS

3.1 INTRODUCTION

The interest in GO after 2004 occurred because it could be used as a means to form single layer graphene, however reclamation of the pristine sp² hybridized structure required the GO material to be reduced.⁷⁸ The conventional methods that were employed to regain this structure include, but are not limited to, reaction with hydrazine,⁷⁹ thermal annealing,⁴⁹ and ultra-violet (UV) exposure.⁸⁰ Now that there is interests in using GO itself, specifically in chemical sensors⁸¹ and optoelectronics,⁸² and thus it is beneficial to understand how reduction techniques can be used to modify the GO structure for these desired applications. The conventional methods of reduction have been thoroughly investigated and are introduced in the following sections. The insights from these GO reductions are used as a metric of comparison for the GO irradiation in-situ experiment results discussed in section 3.3.

High energy ionizing irradiation studies are performed in-situ so that the radiation chemical change, or *radiolysis*, to the GO structure can be measured independently of the other reducing conventions. Some studies have shown that GO can undergo a change in chemistry at standard room temperature and pressure,⁸ from a camera flash⁸³ or sunlight,⁸⁴ and interaction with water vapor.²⁶ This meta-stability of GO requires creative solutions for characterization techniques that can isolate the material from undesired effects. Using an ultra-high vacuum chamber in x-ray characterization techniques as both the reaction vessel and the analysis chamber minimizes these extraneous effects.

The radiolysis of GO is studied using three different categories of ionizing radiation: high frequency electromagnetic radiation (x-ray and gamma radiation), charged particle radiation (alpha particles), and neutron radiation (thermal neutrons). The excited and ionized species in a specific material are independent of the type of high energy ionizing radiation, therefore it is expected that each radiation source would induce similar chemical changes but at different rates. ⁸⁵ The specific excited species as a result of higher energy ionizing radiation is not known for GO. Also the degradation rate of GO chemistry for each

of these ionizing radiation sources is not known. The rate of degradation is not directly related to the energy absorbed by each ionizing radiation because some interaction can result in secondary radiation effects, which do not alter the chemistry.⁸⁵ Because these techniques are measured in-situ, there is near complete control over the energy deposited into the GO system and the time at which measurements are taken. In all, this setup allows for unique characterization of GO chemistry as a result of isolation from uncontrolled reduction, and stepwise energy deposition. Other work that has investigated GO chemistry in a slowed reduction rate environment utilized hydrazine vapor.⁷⁹

3.1.1 Hydrazine Interaction with GO

Hydrazine (N₂H₄) is a highly toxic substance and that is chemically unstable.⁸⁶ Some of the uses for hydrazine include propellant for rocket fuel and as vapor for the reduction of metal oxides. ^{87,88} The benefits of using hydrazine as the reduction agent is that the byproducts from the reduction are nitrogen gas and water.⁸⁸ A recent paper by Mathkar et. al.,⁷⁹ used hydrazine as the means to reduce GO paper and the reaction was slowed during the reduction process to analyze the chemical structure of GO at varying stages. Using attenuated total reflectance fourier transform infrared (ATR-FTIR) measurements they were able to determine exactly which species were removed from the GO structure and at which stage they were removed.⁷⁹ They determined that the hydrazine reduction process initially removes carbonyl and phenol functional groups, followed by removal of the epoxides, and lastly the tertiary alcohols are removed after prolonged hydrazine (Figure 37).⁷⁹ This data from ATR-FTIR is correlated with the change in the C/O ratio as determined from XPS (Figure 37b).⁷⁹ Using UV-Vis, the optical band gap was also measured as a function of hydrazine reduction (Figure 37a).⁷⁹



Figure 37 - Using ATR-FTIR, UV-Vis and XPS Mathkar et. al.,⁷⁹ were able to determine which species were removed from GO, the decrease in the optical band gap (a), and the overall change in C/O ratio(b) as a function of hydrazine reduction.⁷⁹

The optical band gap in Figure 37a is limited to a minimum value of 1 eV, which is what has been found previously in other hydrazine reduction studies.⁸⁹ This minimum reduction is due to the mild nature of hydrazine vapors as a result of minimal penetration into the GO structure.⁸⁹ Another reason this optical band gap is not reduced below 1 eV may be due to the nitrogen substitution that occurs during hydrazine reduction which forms nitrogenbased moieties into GO.⁷⁹ However, the mild reduction from hydrazine vapor allows for the functional groups responsible for the transition into each regime to be identified. It must be noted, however, that the order of functional group removal proposed by Mathkar et. al.,⁷⁹ is specific to interaction with hydrazine vapor. The reduction process for hydrazine vapor with GO requires a multitude of mechanisms that are not well understood, but primarily are a result of isomerization, substitution, and fragmentation.⁹⁰ The interaction process for thermal reduction is entirely different.

3.1.2 Thermal Reduction Process

Scission and rebonding during thermal annealing of organic materials is through pyrolysis (dissociation of bonds caused by heating).⁷⁹ The challenge is understanding the specific interaction and inter-play of the functional groups during the annealing process. Using temperature programmed desorption (TPD) along with mass spectrometry, both the

kinetics during thermal annealing and the specific byproduct species are identified (Figure 38).¹⁰ These measurements were taken from multi-layered GO film on a substrate with a heating rate of 30°C/min, which is shown in the inset of Figure 38a.¹⁰ The gaseous byproduct species that is first developed during thermal reduction is water vapor (m/z = 18) and this out-gassing is initiated at ~70°C.¹⁰ The primary desorption occurs at 130°C, which is the result of the C-C backbone breaking, causing a significant loss of oxygen functional groups to be removed simultaneously. ¹⁰ Another significant finding from this TPD measurement is that no O_2 formation occurs during the reduction process and instead a large majority of desorption contains carbon ($CO_2 = 44$ and CO = 28), which signifies a loss in the carbon backbone structure.¹⁰ Lastly, it is determined that the desorption process is second-order and therefore an intermediate stage is required before the species is removed from the GO structure.¹⁰



Figure 38 - TPD and mass spectrometry are used to identify the byproduct species during thermal annealing. Primary gaseous components are measured (a) $H_2O = 18$, $CO_2 = 44$, CO = 28, and $O_2 = 32$, as well as cracking components (b) OH = 17, O/CH₄ = 16, and CH₃ = 15. The inset in Figure 38a is the heating rate.¹⁰

One important discovery from the TPD study is that GO can decompose at temperatures as low as 70°C.¹⁰ Other work that further investigated this meta-stability of GO at room temperature uses XPS⁸ and FT-IR¹¹ to directly measure the change in the GO structure. Kim

et. al.,⁸ report that at 26±1°C in a dark environment GO underwent spontaneous chemical reduction and the relaxation time was approximately 35 days. XPS is used to identify a significant change in oxidized carbon (Figure 39a) from 64% to 28% after 70 days in a room temperature, humidity controlled chamber.⁸ This is a significant change in chemistry, however it should be noted that the GO used in [Ref 8] is quite different from the traditionally prepared GO.⁸ The material used in [Ref 8] is epitaxial graphene from the carbon face of SiC and is then oxidized using the Hummers method.⁸ There is no discussion of the amount of sulfur in the composition, which could have had a significant impact on the chemical structure of GO as discussed previously. Kim et. al.,⁸ also found very little intercalated water present in the GO structure, however there is limited cleaning of the GO sample after the oxidation process, which may explain the limited water intercalation (< 3% wt.). Density Functional Theory (DFT) calculations are also compared to the results from Kim et. al.,⁸ and show that the formation of hydroxyl groups from free water is more energetically favorable than the formation of epoxide at room-temperature (Figure 39b&c).



Figure 39 - Kim et. al.,⁸ show that GO is not a stable structure at room-temperature conditions (a), where P_{G0} peak is oxidized carbon and P_G is unoxidized carbon. Their work also shows that at room-temperature conditions water present in the structure is more likely to form hydroxyl functional group through diffusion phenomena of C-H species than epoxide functional group formation through experimental (b) and theoretical (c) results.

The other study of the GO structure at near room-temperature environments used temperature controlled FT-IR measurements.¹¹ The multilayer material GO started to decompose at lower temperatures (~125°C) than single layer GO material (~150°C). ¹¹ The primary decomposition at these lower temperatures is believed to be removal of water species from the multilayer GO structures.¹¹ They also show that carbonyl formation at ~150°C is driven by intercalated water (Figure 40).¹¹ Oxygen removal continues throughout the temperature study but after ~175°C the change in the chemical structure begins to decrease.



Figure 40 - FT-IR measurements of 3 layers of GO show that COOH loss is initiated at 125°C as seen in the (c) spectra, which is referenced to the measurement taken at 100°C. Structural formations and losses are shown to occur at varying temperatures, specifically focusing on carbonyl (C=O), epoxide (C-O-C), and carboxylic acid (COOH) groups.¹¹

Mattevi et. al.,⁹¹ also report that the decomposition of oxygen begins to slow above 220°C (Figure 42). Continued temperature increase up to 1100°C is only sufficient enough to

remove 63% of the oxygen in the GO structure.⁹¹ This suggests that removal of the oxygen is limited by some reduction mechanism. As oxygen is removed the size of the sp2 domain islands grow and it is possible that a network of sp2 domain channels forms, allowing for the overall thermal conductivity to increase.⁹² This would allow for greater heat dissipation and reduce the likelihood of oxygen scission.⁹² Figure 41 demonstrates that the removal of carboxylic acid is minimal and is seemingly unaffected by the thermal annealing process.⁹¹



Figure 41 - Thermal anneal study of multi-layered GO measured via XPS shows a decrease in chemical species change as a function of temperature.⁹¹

Results from Mattevi et. al.,⁹¹ have also been modeled by Bagri et. al.,⁹³ with theoretical measurements performed using molecular dynamics (MD). It was determined from the simulation that the efficiency of reduction was greater for GO material with lower initial oxygen concentrations and with higher hydroxyl/epoxy ratio. ⁹³ They also determined that the carbonyl composition is not reduced further above 500°C due to carbonyl formation by rearrangement of epoxy and hydroxyl groups surrounded by saturated carbon (sp3).⁹³ Bagri et. al., also determined that thermal annealing in a hydrogen environment results in a reduced GO structure with fewer vacancies.⁹³

3.1.3. Electromagnetic Ionizing Radiation Reduction Process

The electromagnetic radiation that has enough energy to ionize matter include ultraviolet radiation (UV), x-ray, and gamma radiation. The interaction mechanism varies as a function of photon energy (Figure 42).⁹⁴ It is possible that lower energy electromagnetic radiation such as infrared, visible, and lower frequency ultraviolet light can lead to bond making or bond breaking, however it is first required that light is absorbed by the material.⁹⁵ The primary interaction mechanism for ultraviolet light with matter results in electronically excited valence electron species that can lead to either photolysis (scission of bonds from photo-excitation of electronic states), photoreaction (formation of new chemical species as a result of photo-excitation), or pyrolysis.⁹⁵ Similarly, interaction of x-rays with matter leads to excited electrons species these electrons are excited from core shells rather than valence electrons.⁹⁶ When the x-ray excites these core shell electrons it can result in a chemical change in the material due to ionization or by heating the sample.⁹⁶ Gamma radiation is radiation with photon energy >0.05 MeV and when the energy is >1.022 MeV, it can induce pair-production from the nuclear field, signifying interaction with the nucleus.⁹⁴



Figure 42 - The mass attenuation coefficient of photon radiation through GO as a function of photon energy is calculated with data from NIST.⁹⁷ The range for X-ray photon energies is highlighted in orange and the range for gamma radiation energies is highlighted in purple.

Another key difference between these varying electromagnetic radiation sources is the mass attenuation coefficient (μ/ρ) for GO, which is inversely proportional to the cube of the photon energy until ~2E-2 MeV (Figure 42).⁹⁷ The mass attenuation coefficient is the amount that a substance interacts with any beam that attenuates and is independent of the density and physical state of the material, but does rely on the composition of the material.⁹⁶ The composition used for the mass attenuation coefficient calculation in Figure 42 was taken from XPS measurements for samples used in the irradiation studies and the hydrogen composition is estimated to be half the value of oxygen, as reported in literature.¹² One primary distinction of the mass attenuation coefficient (μ/ρ) is that it is comprised of two parts; the mass scatter coefficient (μ_s/ρ) and the mass energy-absorption coefficient (μ_a/ρ) for each interaction mechanism:⁸⁵

$$\frac{\mu}{\rho} = \frac{\mu_s}{\rho} + \frac{\mu_a}{\rho}$$
 Eq. 8

The mass energy-absorption coefficient and the flux of photons determines the radiation dose, which is the total energy deposited by a radiation source into a material. Calculating the mass energy-absorption through a material empirically can only be done if the intensity of light transmitted through the absorbing medium is measured. However, models for individual atom energy-absorption coefficients have been calculated.⁹⁷ By weighting the components in a similar fashion as the overall mass attenuation coefficient calculation, the total energy-absorption coefficient is determined for each GO material as a function of photon energy (Figure 43). The energy-absorption coefficient is equal to the mass attenuation coefficient when the photon energy <4E-3 MeV.



Figure 43 - Using the NIST database, the total energy-absorption coefficient for GO is calculated as a function of photon energy. The energy-absorption coefficient is a component of the total mass attenuation coefficient, as shown in Equation 8. The energy-absorption coefficient is used to determine the dose absorbed in the absorbing material. ⁹⁷

3.1.3.1 Ultraviolet Radiation Interaction with GO

The change in chemistry of a substance as a result of visible and UV light radiation is termed photochemistry. One rule of photochemistry is that for any material to undergo a change in chemical structure as a result of radiation, the substance must have the capacity to absorb the radiation.⁹⁵ The probability of a chemical species absorbing light depends on the probability of transition of an electron, which is generally from a molecular orbital ground state to an excited state (two-level system).⁶⁷ There are three possible interactions for the transfer of energy between electromagnetic radiation and matter (Figure 44), which are termed Einstein's coefficient.⁶⁷ The diagram in Figure 44 shows the Einstein coefficient for a two-level system and shows the absorption process (B₁₂), stimulated emission (B₂₁),

spontaneous emission (A₂₁) of an electron from a starting energy state, |1>, to an excited energy state, |2>.⁶⁷



Figure 44 - Two-level energy transitions of an electron from a starting energy state, |1>, to an excited energy state, |2>. The transitions are absorption (B₁₂), stimulated emission (B₂₁), and spontaneous emission (A₂₁).⁶⁷

These transitions account for all types of emission of radiation from an excited state, however in multi-level systems any number of combinations of these transitions can occur. ⁶⁷ Each of these transitions are dependent on the transition dipole moment between each energy state.⁶⁷ The transition dipole moment is dependent upon the overlap of the two wavefunctions for each energy state.⁶⁷ The classical explanation of this from the Franck-Condon principle states that an electronic transition is most likely to occur without movement of the nuclei position in the molecular entity, which would result in a vertical transition from the lower energy state wavefunction to the excited energy state wavefunction (Figure 45).⁶⁷ However, in excited energy states it is often found that the vibrational energies and minimum energy inter-atomic distance is different than the ground state due to different forces.⁹⁵ Bond dissociation occurs from photo-excitation when this minimum energy inter-atomic distance is significantly changed between the two electronic energy states.⁹⁵ Even when bond dissociation does not occur during photonexcitation of an electron to a higher electronic energy state, the characteristics of the species are altered and is considered to be an isomer.⁹⁵



Figure 45 - Frank-Condon energy diagram showing electronic transition from v=0 to v=2 potential well, with a slight shift in the minimum energy inter-atomic distance (q_{01}) .⁹⁸

The allowed transitions in GO have been determined to be a pi molecular orbital to pi antibonding molecular orbital transition (π - π *) associated with the sp² hybridized carbon that is un-oxidized, and a nonbonding molecular orbital to pi anti-bonding molecular orbital transition (n- π *) associated with unpaired electrons from the oxygen in the carbonyl group.⁹⁹ The absorption π - π * transition occurs at 210-240 nm (5.2-5.9 eV) for UV excitation and shifts to higher wavelengths as the GO is reduced and the n- π * transition occurs in the 290-320 nm (3.9-4.3 eV) range.⁹⁹ There is also a larger absorption band associated with the size of sp² hybridized carbon clusters that extends from 320 nm up into the visible range.⁹⁹

Plotnikov et. al.,¹⁰⁰ determined theoretically that UV light causes photo-dissociation of the C-O bond from the epoxide (2.1 eV) and tertiary alcohol groups (0.7 eV). It was also determined that C=O and OH groups are photo-eliminated after the formation of intermediate species and that epoxy and hydroxyl groups would migrate to the periphery of the GO plane.¹⁰⁰ This modeled interaction was tested by Stroyuk et. al.,⁹⁹ who

determined that oxygen functional groups were removed with UV radiation and that the sp² carbon cluster area in GO was extended during reduction. The photoreduction did not occur when wavelength (λ) > 460 nm, which is where only sp2 carbon clusters absorb, therefore the n- π^* transition is the absorption that makes the reduction achievable. ⁹⁹ Additionally, water was reported to be a reducing agent during photoreduction and that the key to the reduction may lie in the delivery of energy between water and GO.⁹⁹ UV reduction is not presented in this thesis, but the structural and chemical change of the GO as a result of this photoexcitation is used as a reference.

3.1.3.2 X-ray Interaction with GO

X-ray interaction with a substance is not considered to be a study of photochemistry, but rather radiolysis.⁸⁵ X-ray radiation has enough energy to cause electronic excitation to a more highly excited state, however as the wavelength of light decreases the probability that this radiation will interact with the electron cloud of a species also decreases (Figure 43).⁹⁶ Another mechanism for radiation damage from x-ray is through localized heating. One unique difference between thermal damage and electronic excitation is the rate of chemical change as a function of radiation dose. ⁹⁶ Electronic excitation-driven processes increase linearly with the total dose, unless there is a significant presence of second-order interactions.⁹⁶ Thermally driven processes often involve a variety of heat flow mechanisms and therefore are often non-linear reactions.⁹⁶

The mechanisms for electronic excitation from an X-ray also vary slightly from UV radiation because of the increased energy of each photon. The photoelectric absorption is dominated at lower photon energies and the probability relation (τ) is defined as:¹⁰¹

$$\tau = const * \frac{Z^n}{E_p^3}$$
 Eq. 9

Where Ep is the photon energy, Z is the atomic number and n is a constant that changes as a function of the photon energy.¹⁰¹ The photoelectric absorption is still a significant mechanism for X-ray as shown in Figure 43, but the mass attenuation of the photoelectric absorption in the UV range is four orders of magnitude greater.¹⁰¹ However, there are
additional modes of interaction (coherent and incoherent scattering) that occur for x-rays that do not occur for UV radiation. Coherent scattering is the complete absorption of an x-ray by an electron, which is followed by re-emission of the x-ray with identical energy as the original x-ray. ¹⁰¹ This interaction transfers zero net energy to the atom, but does re-emit the x-ray in any arbitrary direction and attributes to the mass scatter coefficient.¹⁰¹ The incoherent scattering, which will now be referred to as Compton scattering, grazes weakly bonded outer shell electrons and the elastic collision results in the ejection of the x-ray after this collision is primarily in the forward direction, but lower energy x-rays (100 keV) scatter isotropically.¹⁰¹ It is possible for multiple Compton scattering events to occur in a material.¹⁰¹

As the excited electron from Compton scattering cascades through the sample, other secondary electrons are excited, until it eventually releases its excess kinetic energy (thermalisation).⁹⁶ The energy that is transferred to the electron from the Compton scattering event dictates the stopping range of the particle as well as the linear energy transfer. ¹⁰¹ The primary electron beam as well as the cascade of secondary electrons is the primary component for radiation damage from x-rays.⁹⁶ The kinetics of interaction and the specific chemical change as a result of the combination of photoelectric absorption and Compton scattering from x-rays have not been studied for GO. This has a great impact on those who utilize any x-ray technique to characterize GO.

3.1.3.3 Gamma Radiation Interaction with GO

X-ray energy ranges from 0.12 – 50 keV, and gamma radiation refers to photon energies > 50 keV.⁹⁶ Like x-rays, lower energy gamma radiation also interacts with material through photoelectric absorption and Compton scattering (Figure 43).⁹⁷ However, the photoelectric absorption is not the dominant interaction mechanism at energies >20 keV, unless there is significant water presence in the material.⁹⁴ The third mechanism of interaction with matter for gamma rays is pair production, which only occurs for energies > 1.02 MeV.⁹⁴ The electron-positron pair are excited in the usual absorption processes, however the excited positron will recombine with an interacting electron if enough thermal energy is generated

in the system and the recombination will form two 0.51 MeV gamma rays.⁹⁴ Just like excited species from other forms of interaction, the isomer species can interact with surrounding species and alter their bonding.⁹⁷Gamma rays do not have a high interaction probability with lower atomic number materials, unless they are significantly hydrated. Using the trend seen in Table 18, it is estimated that the energy-absorbed coefficient is 44% of the total mass attenuation coefficient for GO.

3.1.4 Beam Particle Interaction with GO

3.1.4.1 Charged Particle Interaction with GO

Charged particles such as alpha particles have very large linear energy transfer (LET) values, amount of energy transferred divided by particle path length, because their velocity is much slower than electromagnetic sources.¹⁰¹ As the mass and charge of the ion increases, the path length decreases. ¹⁰¹ When the heavy charged particles interact with the electric field the charged particle transfer energy and during ionization the particle losses velocity.¹⁰¹ As the alpha particles slow down the specific ionization increases because there is increased interaction time, until a maximum ionization is reached (referred to as Braggs peak) and then the alpha particle rapidly losses energy thereafter until it is extinguished. ¹⁰¹ This stopping range is calculated for each heavy charged particle in GO using a modeling program called Stopping and Range of Ions in Matter (SRIM).

3.1.4.2 Thermal Neutron Interaction with GO

Because neutrons have no charge, they can only indirectly induce ionization in matter. The mechanism of interaction that can generate ionizing particles (protons and heavy positive ions) for thermal neutrons (~0.025 eV) are elastic scattering and absorption (Figure 46).¹⁰¹ A recoiled nucleus, after elastic scattering with a neutron, acts in a similar manner as heavy charged particles. When a thermal neutron is absorbed by a target element it produces an isotope, however the GO neutron absorption cross section is less than 10⁻² barns for thermal neutrons. This is an incredibly low interaction probability for neutrons in GO and it

is expected that no noticeable change in chemistry in GO will occur as a result of the neutron irradiation.



Figure 46 - Neutron interaction with the primary elements found in graphene oxide. The cross-section is a measurement of the likelihood of interaction with the absorbing material. The cross-section value for neutrons in GO is 3-7 orders of magnitude smaller than any of the other radiation sources investigated in this research. Hence it is unlikely that a significant change in chemistry will be noticeable as a result of the neutron interaction.

3.1.5 XPS Studies

Because XPS is the primary tool of investigation for chemical change as a function of radiation, it is important to discuss the viability of peak component fitting in an insulating material. Insulating materials analyzed in XPS with a monochromatic x-ray source require charge neutralization to be performed because these x-ray sources do not produce low energy electrons like an un-monochromatic x-ray source does, which means charge will

build up at the surface of the insulating sample.⁶⁴ Therefore charge compensation has to be performed during analysis of GO, which is an insulating material. The use of an electron flood gun generates electrons at the surface of the measured sample and acts as a conductive film, allowing for trapped photoelectrons to migrate away from the surface of the material. ⁶⁴ This reduces differential charging that can occur in insulating samples, however it can also reduce the binding energy of core electrons in the sample because the work function (ϕ) of the instrument XPS is increased (Eq. 10).⁶⁴

$$E_{binding} = E_{photon} - (E_{kinetic} + \phi)$$
 Eq. 10

Therefore, the spectral centers of each photoelectron peak need to be corrected for this shift in energy. A database of XPS analysis has shown that aromatic sp² carbon has a core electron binding energy of 284.8 eV.⁶⁴ This is the same binding energy for adventitious hydrocarbon that is often found on many samples.⁹⁶ Assigning the sp² carbon peak can be difficult because there are other organic functional groups that show up near this peak (Table 19), which can create an entire parent peak with multiple photoelectron origins.

Table 18 - Carbon 1s component peak positions are listed as the relative change in binding energy incomparison to the sp² aromatic carbon peak.⁶⁴

Functional Group	Chemical Shift (eV) Relative to aromatic sp ² carbon			Reference
		(284.8 eV)		
	Min (eV)	Max (eV)	Mean (eV)	
Hydroxyl (C-OH)	1.49	1.75	1.57	64
Epoxide (C-O-C)	1.35	2.2	2.04	64, ¹⁰²
Carbonyl (C=O)	2.83	2.99	2.92	64
Carboxylic Acid (O=C-OH)	4.2	4.35	4.28	64
(° ° ° ° í)	0.23	0.54	0.30	64
	0.23	0.34	0.39	04
C-SO ₂	0.32	0.66	0.40	64

Amorphous C-C sp ³	0.6	0.95	0.9	64

One method through which accurate peak fitting can be performed is by cross-checking the core line positions of other elements in these carbon compounds. There are only three other possible elements that are present in GO, which include oxygen, sulfur, and hydrogen as seen in previous XPS analysis (Figure 26 & 32). However, the binding energy of hydrogen is extremely low (13.6 eV), which is in the region where valence electrons from other species show up.¹⁰³ Therefore, only oxygen and sulfur are distinguishable in XPS measurements. The component peak location relative to the charge corrected sp² aromatic carbon for oxygen and sulfur are given in Table 20 and 21, respectively. As mentioned in section 2.3.2.4, it is likely that both an organic sulfur compound and sulfuric acid are the remaining sulfur species in GO. The peak positions for sulfuric acid are previously mentioned in Table 12.

Functional Group	Binding Energy w/ charge shift (aromatic sp ² carbon		Reference	
		284.8 eV)		
	Min (eV)	Max (eV)	Mean (eV)	
Water (H ₂ O)	533.1	534.8	533.5	104, 105
Hydroxyl (C-OH)	531.7	533.84	532.77	64, ¹⁰⁶
Epoxide (C-O-C)	533.18	533.65	533.45	64
Carbonyl (C=O)	-	-	531.45	64
Carboxylic Acid	531.82	531.90	531.85	64
(O=C-OH)		002170	22100	
-SO ₂ -	531.60	532.40	532.00	64

Table 19 - Oxygen 1s component peak position are listed as the binding energy corrected for chargingusing the sp² aromatic carbon peak position.64

3.2 EXPERIMENTAL

Several new characterization techniques were utilized to determine the change in chemistry as a function of radiation. Some of the previously mentioned techniques from section 2.1 were used again but with a different setup or parameters. The following explains the techniques used, the radiation sources, calibrations to determine radiation dose and setups required for characterization.

3.2.1 In-situ XPS

GO paper samples, GO5 and GO12, were irradiated inside the vacuum chamber of the XPS system (3E-8 Torr) during the x-ray irradiation study. The x-ray source for the in-situ irradiation study was the Al K-alpha monochromatic x-ray source used in the XPS (1486 ev). The number of K-alpha photons produced by an electron of energy E_0 incident on the Al anode (Z=13) into a solid angle of 4π sr is given by the following equation:⁶⁵

$$Q_{(E_o,Z,hv)} = 3.48E4 \ \frac{\omega R}{Ac} (U_o - 1)^{1.67}$$
 Eq. 11

Where ω is the fluorescent yield, R is the backscattering of electrons, A is the atomic weight of the target x-ray anode element, c is a constant (2.7E4 keV m2 kg-1).⁶⁵ The overvoltage, Uo, is a function of the critical excitation energy for the K shell of the target element (Ec) and the incident electron energy (Eo).⁶⁵ Briggs (2003)⁶⁵ calculated the quantum efficiency for Al K-alpha with an incident electron energy of E₀ = 15 keV and electron beam spot size to be ~2 mm diameter, to be 3.6E13 photons/cm²/s. The energy of the Al K-alpha x-ray source during the XPS measurements presented here was 14 keV and the critical activation energy for aluminum E_c = 1.559 keV.¹⁰⁷ It is assumed that all other parameters ($\frac{\omega R}{Ac}$) for the quantum efficiency calculation for Al K-alpha in the Kratos Axis Ultra are identical to the calculated Al K-alpha source in Briggs (2003). ⁶⁵ Therefore the flux of K-alpha photons at an E₀ = 14 keV is 3.2E13 photons/cm²/s. The starting energy-absorption coefficient for GO5 and GO12 were identical (1.09E3 cm²/g) because the compositions were very similar. Using both the flux of x-rays and the total energy-absorption coefficient at 1486 eV, the rate of energy absorbed per unit mass by an irradiated material was calculated from Eq. 12 to be 8.3E3 Gy s⁻¹(or J kg⁻¹ s⁻¹). This value is known as the absorbed dose rate (D_{AR}).¹⁰¹

$$D_{AR} = \varphi_p * E_p * \left(\frac{\mu_a}{\rho}\right)$$
 Eq. 12

Where μ/ρ is the mass attenuation coefficient, φ_p is the particle flux of the radiation source incident on the GO sample and Ep is the photon energy.¹⁰¹ Because the x-ray source was also used for analysis, spectra could be continuously measured during the entire irradiation process of GO. The C 1s spectra scan width was 12 eV with a step size of 0.1 eV and a dwell time of 2000 ms. The only different parameter for the O 1s spectra scan was that the width was 10 eV. It took 205 seconds to scan the C 1s spectra, and 171 seconds to scan the O 1s spectra. The time between each C 1s and O 1s spectra was 53 seconds and the time for the detector channels to reset and commence the second run of each spectra took 57 sec. During this entire period the x-ray is on and is irradiating the GO sample. Therefore the time resolution for each spectral measurement during the x-ray exposure was 486 seconds, which is a total dose absorbed of 4 MGy.



Figure 47 - Set of radioisotopes from spectrum techniques. The set includes Cs-137, Co-60, Sr-90, Tl-204 and Po-210. Each disc is 1" in diameter and all radioisotopes are completely sealed in the epoxy except for the Po-210 source.¹⁰⁸ A laminated disc with a 2 mm diameter disc source of Co-60 was one radioisotope from a set of sources purchased from Spectrum Techniques (Figure 47) and was used for the insitu gamma irradiation XPS measurements. The energy of the Co-60 photon is 1.25 MeV and the energy-absorption coefficient for GO at this energy value is $2.71E-2 \text{ cm}^2/\text{g}$. This source had had an activity of 1 µCi (3.7E4 Bq). The absorbed dose rate calculation from this disc source is 0.8 µGy s⁻¹, calculated from Eq. 13.¹⁰¹

$$D_{AR} = \frac{CE_p}{2\pi r} * \left(\frac{\mu_a}{\rho}\right)$$
 Eq. 13

Where C is the activity in Bq, Ep is the photon energy, and μ_a/ρ is the energy-absorption coefficient.¹⁰¹ The 1 µCi Co-60 radioisotope source was mounted onto the stage holder in the XPS and was completely sealed in a laminate plastic disc. It was initially tested in the analysis chamber without the x-ray gun on and no secondary excitations were picked up from the detector. The GO sample could be mounted over top the Co-60 source, 1 mm away from the source with the plastic laminate acting as a barrier. Because the GO samples are insulating, the GO and the radioisotope disc were wrapped in aluminum foil with a hole cut out over the paper and radioisotope (Figure 48b). Therefore the ionizing radiation attenuates through the entire GO paper and only the backside (relative to the radioactive source) is measured by the XPS system. The attenuation of gamma rays is minimal relative to the thickness of the GO paper, therefore there was no limit to the thickness of the paper but the thickness was still recorded in order to account for any attenuation that occured.⁹⁷ In between XPS measurements the setup was held in the load lock chamber rather than the analysis chamber to avoid any damage to the charge neutralizer system, detector, or x-ray gun. The spectra was taken at periodic intervals in the analysis chamber and then placed back into the load lock chamber.



Figure 48 - Setup for the radioisotope in-situ XPS measurement. The XPS load lock chamber was used as an isolated vacuum chamber in between XPS measurements (a). The radioisotope laminated disc source and the GO paper are wrapped in aluminum foil and mounted onto the XPS sample mount bar (b).

The in-situ alpha source was a polonium-210 alpha (5.3 MeV) with an activity of 0.1 μ Ci. Using the Stopping Range of Ions in Matter (SRIM) program it was determined that the stopping range for GO was 26±0.5 μ m depending on the specific composition of the GO material. The Bragg peak is at 24±0.5 μ m, therefore the absorption/interaction of alpha in GO is optimized by tailoring the thickness between 23-25 μ m. The setup of the source was identical to the Co-60 in-situ measurement.

Degradation rates for each irradiation study were calculated from the entire integrated peak area for each spectra. The background fits for each carbon 1s and oxygen 1s spectra were Shirley background fits and the cut-off values were 278-290 eV for the carbon 1s spectra and 525-535 eV for the oxygen 1s spectra. These ranges for the background fits are before charge shift is performed.

3.2.2 X-ray Excited Optical Luminescence (XEOL)

This characterization technique uses the same Beer-Lambert absorption principle and the x-rays generate photoexcitation as well as Compton scattering of electrons. The energy transferred to a material during the cascade of electrons can cause structural damage and this structural damage acts as a luminescent center.¹⁰⁹ Luminescent centers are types of

color centers and can be the result of point defects in a crystal or as a result of an activator in the structure.¹¹⁰ The luminescent centers can be simple point defects or single activator atoms, or they can be more complex cluster of defects or activator atoms.¹¹⁰ The defining characteristic of a luminescent center is absorption of light in a spectral region that eventually leads to radiative recombination of excited particles at a drastically different energy, causing emission in a separate spectral region.¹⁰⁹ In XEOL, light emissions are monitored from the optical region (UV, visible, and near-infrared) on absorption of x-rays, often tunable from a synchrotron light source. ¹⁰⁹

The XEOL and synchrotron source used for the measurements of GO were performed at Argonne National Laboratory in the Advanced Photon Source facility. The tuned x-ray source was 800 eV. This lower x-ray energy allowed for the decay rate of the luminescence signal to slow down to several minutes and could therefore be detected by the monochromator. The signal intensity was increased by setting the monochromator to zero order. The overall x-ray flux density was 5.3E14 photons/second/cm². The total energy absorbed coefficient for the x-ray source during this irradiation was calculated from the NIST database and is determined to be 5.4E3 cm²/g. Therefore using Eq. 12 it is determined that the D_{AR} is 366.8 kGy s⁻¹, which is 44 times greater than the D_{AR} in the XPS system. The excited area radius during analysis depends on the band gap of the material, but often varies from 10-50 nm.¹¹¹ Therefore it is a semi-site selective characterization technique.

3.2.3. X-ray Absorption Near Edge Structure (XANES)

The principle of XANES is very similar to XPS, where both depend on the absorption of xrays leading to the photoexcitation of a core electron. However, XANES analyzes the change in absorption of x-rays as the energy of the x-ray is scanned through the binding energy of the element of interest.¹⁰⁹ The change in absorption is measured by the x-ray fluorescence that occurs during the recombination of an excited core hole state (Auger electron emission is the other possible mechanism after core shell electrons are emitted).¹⁰⁹ The XANES was performed at Argonne National Laboratory in the Advanced Photon Source facility in the same chamber as the XEOL. Only the oxygen K-edge absorption edge structure was measured for GO12. The species in the starting oxygen Kedge absorption spectra was compared to the species present after a 2hr XEOL irradiation.

3.2.5 Monte Carlos Analysis

Monte Carlos Analysis was used to determine the transfer of energy from the gamma radiation. The simulation was performed using MCNPX. The modeled GO had a density of 1.8 g/cm^3 , had a thickness of $10\mu\text{m}$, and the molecular formula used was $C_8H_2O_4$. The gamma source was a point source of gammas and the total number of particles simulated was 1E7, which is slightly more than the particle flux for the gamma radionuclide source used (3.7E6 photons/sec). Mesh tallies were made for the number of transmitted gamma particles, the number or free radicals formed and the linear energy transfer per electron particle track.

3.2.4 Neutron Transmission Measurements

The neutron radiation study could not be done in-situ with XPS. A thermal neutron radiation source was used at the Breazeale Reactor Center at PSU, and the transmission of neutrons through GO16 paper was measured. The energy of the thermal neutrons was 0.025 eV. The power of the reactor during measurements was 800 kW, which resulted in a flux of 4.3E7 n/cm2/sec. The variance in the neutron flux was $\pm 1\text{E6} \text{ n/cm2/sec}$. The total exposure time was 1 minute. The thickness of the GO material was 20 µm and the size of the GO paper was 5x5 cm. The diameter of the neutron beam was 2 cm and the GO paper was aligned to the center of the neutron beam. The GO material was transported via a sealed vacuum bag, which was stored inside of an opaque container to limit the interaction with UV light and water vapor in the atmosphere. A control sample was also brought along and was exposed to air during the same duration of the neutron exposure. Both GO materials were then re-sealed in vacuum bags and transported to the XPS. These two materials were analyzed in XPS before and after the irradiation and transfer time from the sealed bags to the XPS chamber was kept to a minimum.

3.3 RESULTS

3.3.1 X-ray Irradiation

3.3.1.1 In-situ XPS

Identifying interaction mechanisms during reduction of GO requires isolation from other reducing environments. The work presented here utilizes the ultra-high vacuum chamber in XPS as a means to isolate GO and study the radiolysis. Two samples were measured during the x-ray in-situ reduction process, GO5 and GO12. As a reminder these materials were both from NF50 parent material but oxidized using different methods; GO5 was oxidized using Hummers method⁴² and GO12 was oxidized via Tour's method¹⁶. Previous analysis of these two materials in XRD (Figure 22 and Table 14), FT-IR (Figure 36), XPS (Figure 25), and AFM (Figure 31) reveals near identical chemical structure as well as similar flake size. However, analysis of GO during slow reduction can reveal in depth detail of chemical structure and therefore these samples are analyzed to determine any discernible distinction between the two materials.⁷⁹ The survey spectra is measured before high resolution measurements and reveals that both samples have < 0.7 % sulfur content and there are no other contaminants (Figure 49).



Figure 49 - The XPS survey spectra for both GO5 and GO12 highlight no other contamination other than the expected minor sulfur content (GO12 S 2p % = 0.65, GO5 S 2p % = 0.38). The insets show a zoomed in window of the survey spectra highlighting the sulfur photoelectron peaks from the 2s and 2p electron.

The first goal of the in-situ x-ray irradiation analysis was to determine the rate at which degradation of the GO chemistry takes place. After irradiating GO5 for nearly 21 hours, XPS measurements show that the degradation rate for the material is non-linear (Figure 50). However, it was not until this extended irradiation study was performed that this nonlinear exponential decay rate was observable. Previous x-ray in-situ irradiation measurements totaled 160 MGy, and when a best fit line is performed for this extended GO5 measurement from the interval of 0-160 MGy the relationship is linear (Figure 51). The reason for this discrepancy in decay rate is that this analysis is a comparison of the total O/C ratio as a function of absorbed radiation. It is likely that only specific oxygen functional groups are removed during the irradiation process. Therefore the decay constant from this 0/C degradation ($\lambda = -0.002$) is likely a combination of the different species decay constants. If a double exponential decay fit is performed the correlation coefficient is increased marginally (mono-exponential decay = 0.9954, double exponential decay = 0.9958). The decay constants from the double exponential decay are λ_1 = -0.0012 and $\lambda_2 = -0.0029$. Both of these fits have a baseline offset, which signifies complete oxygen removal is not possible during x-ray irradiation. Previous thermal reduction experiments and models have shown that there is re-formation of carbonyl groups which limits only 63% of the total oxygen to be removed during reduction.^{91,93}



Figure 50 - The degradation rate for GO5 as a function of absorbed x-ray irradiation. The value X = O/C ratio, where Xo is the initial O/C ratio and Xa is the O/C ratio after 'a' amount of radiation is absorbed. One linear fit is matched to degradation data from 0-160 MGy and the exponential decay fits are performed for degradation data from 0-640 MGy. The R² value indicates that the data from 0-640 MGy best fits a double exponential decay.

The asymptotic limit for the Xa/Xo ratio is 0.66-0.69, which translates to 31-34% oxygen removal from GO. If an exponential decay fit is performed for the linear section of the GO5 degradation data (0-160 MGy) the asymptotic limit for the Xa/Xo ratio is 0.80. Therefore, exponential decay fits for previous runs with shorter irradiation times are likely an underestimate of the total potential oxygen removal and only linear fits are performed to compare the data (Figure 52). The outliers in Figure 51 at around 220 MGy and 370 MGy are discussed in Appendix H.



Figure 51 - Degradation calculation for GO5 and GO12 from XPS analysis. Dashed lines are runs with measurements up to 160 MGy and solid lines are measurements up to 300 MGy. Xo is the initial O/C ratio and Xa is the O/C ratio after 'a' dose absorbed in MGy. The degradation rate seemingly follows linear fit, however figure 50 shows that when the irradiation is performed for longer duration the data best follows a double exponential decay.

Line fits for repeat measurements GO5 and GO12 that were only irradiated up to 160 MGy (GO5_B and GO12_B are dashed lines) or 290 MGy (GO5_A and GO12_A are solid lines) are shown in Figure 52. The linear fits show that both GO12 samples had a degradation rate of ~4.5E-3 Xa/Xo/kGy. The GO5 sample in Figure 51 is represented in Figure 52 as the GO5_A solid black line with only measurements from 0-290 MGy included. The linear degradation of this sampling of data points for GO5_A results in a degradation rate of 5.1E-3 Xa/Xo/MGy. This near match of the degradation for GO12 samples and the GO5_A solid line sample suggests the species targeted by radiolysis has nearly the same composition in each measured material. The GO5_B had a slower degradation rate (1.3E-3 Xa/Xo/MGy), which suggests that targeted species during radiolysis had a much smaller composition than the other measured materials. To determine which species are being targeted during irradiation, high resolution spectra for both the carbon 1s and oxygen 1s photoelectron peaks are analyzed (Figure 53).



Figure 52 - High resolution C 1s (a) and O 1s (b) spectra for GO5_A with charge shift. The peak position regions for each potential carbon compound are boxed in both spectra. The boxed regions for C 1s have multiple peaks in each region: R1 = carbon sp2 + carbon sp3 + covalent sulfate (C-SO₂), R2 = carbonyl (C=O)+ epoxide (C-O-C) + hydroxyl (C-OH), and R3 = carboxylic acid (O=C-OH). The boxed regions for O 1s include R4 = epoxide + hydroxyl + water and R5 = carboxylic acid + carbonyl+ covalent sulfate.

Spectra after the first and last run (4 MGy and 640 MGy) are compared to show the change in carbon compounds in GO5_A. The results from this reduction show that the carboxylic acid (O=C-OH) group, R3, is nearly unchanged throughout the reduction, which matches with the shift in the oxygen 1s peak towards the C=O peak region. The most convoluted peak region in the C 1s spectra is R2, which could be represented by three different functional groups (carbonyl, epoxide, and hydroxyl groups). The contributions of core photoelectrons for each of these compounds to both R2 and R4 are:

$$C 1s: R2 = 2Peak_{epoxide} + Peak_{carbonyl} + Peak_{hydroxyl},$$
 Eq. 14

and

A combination of these species are the primary targeted compounds during irradiation reduction. The peak position for R2 shifts from 287.1 eV down to 286.8 eV after the 640 MGy irradiation (Figure 53). Carbonyl species are found at higher binding energies than the C-O species. This signifies that there are at least two component peak fits in the R2 peak; one peak most likely representing carbonyl species and then the other peaks would represent the C-O species. The shift of R2 also represents a reduction in the carbonyl species. This shift is seen for each GO x-ray irradiated material. The shift of the R2 peak for each GO material after 160 MGy is shown in Table 21.

GO Sample	Carbon 1s R2 peak shift @ 160 MGy (eV)
GO5_A	-0.18
GO5_B	-0.12
G012_A	-0.11
G012_B	-0.20

Table 20 - Peak shift for the central peak in the carbon 1s spectra indicating a loss of C=O species



Figure 53 - R2 peak position (black solid line) for GO5_A during x-ray irradiation process shifts closer to the C-O species. The dotted red lines are the NIST reference peak positions for each respective species.

The minor differences in the peak shift and degradation rate between each GO sample measured during the x-ray irradiation are possibly a result of slight carbonyl composition variation. To determine the exact carbonyl composition for each GO material component peak fitting was performed. To determine the accuracy of the peak fitting for this highly convoluted peak region, multiple fitting parameters were tested for each carbon 1s peak in Figure 52. These fits were tested against multivariate analysis, previous FT-IR measurements, the oxygen 1s spectra, the binding energy ranges for the known species in GO, as well as previously mentioned models (Lerf et. al.,³¹ and Mathkar et. al.,⁷⁹) to compare ratios for the carbon species present. All models and peak positions had a calculated remaining oxygen content (for the model assuming C-OH:C-O-C is 1:1) that was -5.0% or greater, and the residual standard deviation (RSD) was less than 10 (Appendix I). Considering all of these parameters as well as the FWHM, the best fit peaks for the carbon 1s spectra for both the 4 MGy measurement and the 637 MGy measurement of GO5 are compared to yield the composition at each stage (Figure 54).



Figure 54 - High resolution XPS of GO5_A carbon 1s spectra after 4 MGy (a) and 640 MGy (b) with component peak fits and the respective composition for each species.

The C-O peak is a representation of all possible species that have been measured in FT-IR (epoxide, ether and hydroxyl). The high resolution peak fitting confirms that there is a significant increase in the overall C sp2 bonding and that the reduction of carbonyl is greater than the reduction of the C-O species. However, the error in peak fitting for the initial carbonyl peak is 41%. The inaccuracy of peak fitting for is a result of the ratio of sp2 to sp3 carbon binding. Not knowing this ratio significantly affects the peak assignment, because each subsequent peak range is dependent upon the location of the sp2 carbon peak. Also, composition analysis of the specific compounds in R2 is difficult because there may be multiple peaks represented by the C-O peak and the close proximity of the C=O peak to the C-O peaks. The error for each peak fitting is nearly identical for each GO material that was analyzed. The average composition for each peak is shown for each GO material in Figure 55.





Interestingly, the materials from the same GO run have varying chemistry. This reconfirms the necessity for in-situ measurements because the GO chemistry is susceptible to change in any standard room temperature environment. GO5_B and GO12_B had on average 5% more carbonyl species than the samples of the same GO run that were irradiated for longer periods, however the error for the peak assignment for the carbonyl species was $\pm 10\%$. Although this is a large error, each of these materials had a unique chemical alteration during the irradiation process. Both GO5_B and GO12_B had an increase in the total C-O species of 9% and 6%, respectively (Figure 56). Also, as previously mentioned the peak fitting error goes down as the carbonyl species is removed and the error for the GO5_B C-O peak after 160 MGy is $\pm 7\%$ and $\pm 4\%$ for the GO12_B C-O peak after 160 MGy. Therefore, it is likely that the analysis of the average starting composition is qualitatively accurate, even though the difference in the initial composition is less than the error for m peak assignment.

The re-formation of C-O species during the irradiation process is likely a result of carbonyl dissociation or excitation. There are two known C-O bonding species in GO, which are hydroxyl (C-OH) and epoxide (C-O-C) groups.³¹ As mentioned, the shift of the R2 peak in the C 1s spectra moves toward a lower binding energy for each GO material which

indicated a loss of the carbonyl species (Table 21). The results from the peak fitting confirm that the carbonyl species is removed during the irradiation process (Figure 56). In addition, the peak fitting identifies a minor shift in the C-O peak position (Table 22), which could represent the growth of a C-O species at lower binding energies, such as the hydroxyl group.



Figure 56 - Chemical change for each x-ray irradiated sample, including GO12_A (a), GO5_A (b), GO12_B (c) and GO5_B (d). The only difference between the A samples and the B samples is that they were formed into GO paper at different times. Samples A and B are both from the same respective GO suspension (GO5 and GO12). See Table 13 for difference in parameters for these two oxidized materials.

Previous models of GO show that the most stable chemical structure for GO is hydroxyl and epoxide groups paired together, forming a 1:1 ratio.³¹ Using this 1:1 model for the C-O peak, the amount of oxygen bonded to carbon is calculated from the peak fits for each of these species (Table 22). The calculations show that the 1:1 C-OH:C-O-C model for the fitted

peak positions result in nearly 100% of the oxygen present in the structure to be bonded to carbon species. This is unlikely, because FTIR (Figure 36) indicates that water is still present in the structure and the remaining covalent sulfur species may also have a small contribution to the oxygen 1s peak. However, as the GO material is irradiated the amount of oxygen bonded to carbon decreases when using the 1:1 model. If water or the sulfur species was removed from the GO during this irradiation and the carbon containing oxygen functional groups remained constant this percentage of oxygen bonded to carbon would increase. Therefore this decrease in oxygen bonded to carbon is likely related to an increase in the amount of C-OH relative to the amount of C-O-C species. This is because for every core photoelectron from the oxygen in the C-O-C species there are two core carbon photoelectrons. Although the exact ratio of C-OH:C-O-C is not known, other works have calculated the water content to be as much as 10%.¹² This would mean that the amount of oxygen bonded to carbon could be as low as 90%. Assuming that 10% of the oxygen peak originates from water trapped between layers of GO and that it is constant throughout the irradiation suggests that most of the GO materials after the 160 MGy are nearer a 1:1 ratio of C-OH:C-O-C and the starting composition is most likely a higher concentration of C-O-C species (Table 22).

Table 21 – Analysis of the C-O peak position in the C 1s XPS spectra show a shift from C-O-C species to C-OH species. The decrease in the amount of oxygen bonded to carbon also indicates that there must be a relative increase in the C-OH compared to C-O-C.

GO Sample	4 MGy Measurements		160 MGy M	160 MGy Measurements	
	C-O Peak	O bonded to C	C-O Peak	O bonded to C	
	Position	COH:COC = 1:1	Position	COH:COC = 1:1	
	(eV)	model (%)	(eV)	model (%)	
GO5_A	287	99.3	286.92	95.6	
GO5_B	287	100.2	286.95	92.6	
G012_A	287	101.6	286.93	97.5	
GO12_B	287	98.2	286.95	91.4	

These results indicate that the decay of the O/C ratio is not a mono-exponential decay as shown in Figure 50. There are at least two decay processes (carbonyl photodissociation and epoxide photodissociation), which most likely result in gaseous byproducts (carbon monoxide and/or carbon dioxide) as seen from TPD measurements performed by Jung et. al.,¹⁰ as well as the formation of hydroxyl groups. Sample GO5_B shows the greatest change in the COH:COC ratio, which is most likely why it has the slowest O/C reduction rate (Figure 51). It is possible that this GO5 B material had more intercalated water present than the other GO samples, because it had the highest starting O/C ratio out of all the materials analyzed. The work presented by Kim et. al.,⁸ has shown a free water molecule is more likely to form a hydroxyl group than an epoxide group under mild heating conditions. Therefore, it is possible that either the epoxide or water molecule are responsible for the formation of the hydroxyl groups. Another explanation for the slight increase in hydroxyl groups relative to the epoxide groups is the possible reduction of the GO flake size during irradiation. Mathkar et. al.,⁷⁹ showed that tertiary alcohol species (C-OH) form at the edge of graphene oxide planes. It is possible that there is migration of the dissociated carbonyl or epoxide towards the edges of the GO plane to form the tertiary alcohol.

3.3.1.2 XANES/XEOL

One issue with the analysis of the XPS O1s peak is that it is a very broad structure with little detail (Figure 52b). The advantage of using XANES is increased separation between oxygen compound excitation energies. Sample GO12 is irradiated by soft x-rays (800 eV) from the synchrotron source at Argonne National Laboratory. This irradiation is done in-situ and the XANES Oxygen K-edge absorption spectra for GO12 is measured at the beginning and end of the 2hr x-ray irradiation (Figure 57). Two GO12 samples were analyzed using the XANES/XEOL setup, and were not the same samples from the in-situ XPS analysis. The results show both subtle changes in peak positions as well as some dramatic transitions in peak intensity as a result of irradiation. The peak locations from electron transition resonances and their associated oxygen species orbital are assigned in Table 23.



Figure 57 – XANES measurement of the Oxygen K-edge absorption spectra at 66 MGy and 2500 MGy absorbed energy from the in-situ x-ray irradiation for GO12_1 (a) and GO12_2 (b).

The peak intensity for the XANES measurements are referenced to the background line seen from 525-530 eV. The peaks that have the greatest reduction in intensity after the irradiation are peaks *c-g*. The intensity for peaks *d* & *e* have the most noticeable reduction after irradiation, which are assigned to $\sigma^*(O-H)$ and $\sigma^*(C-O)$, respectively. The $\sigma^*(O-H)$ peak could be representative of both hydroxyl species and water intercalated in the GO. The O K-edge spectra after irradiation also shows that the peaks at *a* & *b* shift in intensity. Both of these peaks fall within the range for the $\pi^*(C=O)$ peak excitation energies. It is possible that the lower energy peak, peak *a*, is representative of the carboxylic acid functional group that remains unchanged throughout the 640 MGy x-ray irradiation in XPS. The only slight difference between x-ray absorption spectra for GO12_1 and GO12_2, is that GO12_2 has less of a decrease in intensity for peaks *c-g* after the irradiation, but that is likely because it is irradiated for half as long as sample GO12_1.

Peak Label	Peak Position (eV)	Assignment	Reference
а	531.2	π*(C=O)	102, 112
b	532.0	π*(C=O)	102, 112
С	534.0	π*(C-O)	102, 112
d	535.5	σ*(0-H)	102, 112
е	539.5	σ*(C-O)	102, 112
f	542.5	σ*(C=O)	102
g	544.5	σ*(C=O)	102

Table 22 - Assignment of peak positions in the Oxygen K-edge absorption spectra in XANES (Figure58) for GO.

After the oxygen K-edge absorption spectra was initially measured for both samples, the luminescence from the GO material as a result of x-ray excitation was measured. The luminescence peak for GO12 during the XEOL measurements was centered around 2.4 eV, which is slightly red shifted in regards to luminescent peak energies reported from photoluminescence (PL) spectroscopy (2.85 eV).¹⁵ This is because the process of energy transfer and the excitation of the electron to the conduction band of the species from an x-ray is often different than the excitation from UV light used in PL spectroscopy.¹¹¹

The luminescent peak center of mass for GO12_1 was 2.33 eV and was 2.55 eV for sample GO12_2 (Figure 58). The in-situ XANES analysis of both materials revealed nearly no difference between the bonding species present, however this technique is an integration of the species found throughout the bulk material. The difference in the luminescent peak center is likely a result of slightly varying localized chemistry, because the area of excitation from XEOL is approximately 10-50 nm.¹¹¹ The reduction of the GO material as a result of the x-ray irradiation immediately begins to diminish the luminescence peak intensity (Figure 58). This is the opposite of what has been detected during PL analysis of reduced GO (from both thermal and hydrazine reduction).^{15,59} The PL signal is enhanced

during the reduction of GO because of the confinement of the sp2 domain. ⁵⁹ However, after a certain degree of reduction the sp2 domains re-grow and the PL signal quenches. ⁵⁹ The XANES analysis shows that the removal of the epoxide and carbonyl species results in the reduction of the luminescence peak during the x-ray irradiation. The interaction contribution from Compton scattering is 0.3 times less for the lower energy x-ray (800 eV) used during the XANES/XEOL than the x-ray source (1486 eV) used during the XPS study. It is possible that the carbonyl species is removed as a result of the Compton scattering and therefore results in a smaller change in carbonyl composition during the XANES analysis.



Figure 58-The optical luminescence from x-ray excitation decreases in intensity as a result of irradiation. The variation in the luminescent peak position for each samples indicate a difference in structure.

The decay of the luminescent peak for both materials best fits a double exponential decay, which represents two modes of photolysis during x-ray irradiation. The time constants for the double exponential decay for GO12_1 are $\tau_1 = 826$ seconds and $\tau_2 = 106$ seconds and the time constants for sample GO12_2 are $\tau_1 = 719$ seconds and $\tau_2 = 99$ seconds (Figure

59). The absorption cross section (σ) for each photolysis processes can be calculated according to:⁸⁵

$$\sigma_n = 1/(\tau_n * \phi_p)$$
 Eq. 16

where *n* represents the specific photolysis process and ϕ_p is the flux density of the x-ray. The absorption cross section for G012_1 is $\sigma_1 = 2.3$ Mb (or 2.3×10^{-22} m²) and $\sigma_2 = 18$ Mb and the absorption cross section for G012_2 is $\sigma_1 = 2.6$ Mb and $\sigma_2 = 19$ Mb. The absorption cross-section is closely related to the energy absorption coefficient as shown by the following:⁸⁵

$$\sigma_n = \left(\frac{\mu_a}{\rho}\right) m_a / N_a$$
 Eq. 17

where μ_a/ρ is the energy absorption coefficient, m_a is the atomic molar mass (g/mol) and Na is Avogadro's number. The energy absorption coefficient calculated from each absorption cross-section is specific to the photoylsis of the individual species and the energy of the x-ray used during this analysis. Although the previous analysis from XPS showed that the carbonyl species undergoes photodissociation at a faster rate than the epoxy group, the in-situ XANES measurements show the greatest change for the epoxy group. Therefore it is assumed that the shorter time constant (τ_2) is affiliated with the epoxy species.



Figure 59 - XEOL measurements of GO12_1 (a) and GO12_2 (b) show the luminescence as a result of xray irradiation follows a double exponential decay fit. The y0 is the baseline shift, A1 is the decay amplitude and invTau1 is the decay rate.

The average energy absorption coefficient for epoxy is 7.68E1 g/cm² and the energy absorption coefficient for carbonyl is 9.25E2 g/cm². These energy absorption coefficient values are only 17.1% ($\frac{carbonyl\,\mu_a/\rho}{GO\,\mu_a/\rho}$) and 1.4% ($\frac{epoxy\,\mu_a/\rho}{GO\,\mu_a/\rho}$)) of the total GO energy absorption coefficient. This indicates that the majority of the energy transfer process is not related to the photodissociation of carbonyl or epoxide. This is expected because most energy is absorbed during photoexcitation processes for all species in the GO material.

3.3.2 Degradation Rate from High Energy Radiation

Because the absorbed dose rate (D_{AR}) for the in-situ high energy radiation sources are much lower than the x-ray D_{AR} , the degradation rate from Figure 51 is used to calibrate the XPS measurements. The linear fit for the change in O/C as a result of x-ray irradiation was shown to be an accurate representation of the degradation rate at lower dose absorbed values. The linear fit used to calibrate the following degradation rate calculations is the following:

$$O/C_{x-ray} = 1 - 4.6E^{-}4 \cdot (x \cdot 8.3E^{-}3)$$
 Eq. 18

Where the x value is the time (seconds) that the GO sample is irradiated by x-rays during the XPS measurement. The composition of each region in the C 1s spectra was also analyzed for each high energy radiation study. To account for the change from the XPS measurement an exponential curve fit was matched to the change in each region for GO materials analyzed in section 3.3.1. Regions were analyzed rather than the individual components because the error for the region peak fitting was roughly 1/10th of the error for the component peak fitting. The equations in Figure 60 are used to calibrate the region analysis for the following degradation rates of the various high energy radiation. It is not known why the change in composition follows a second order polynomial initially and then best matches an exponential decay/growth equation. It is possible that there is a certain threshold of incident x-ray photons required before the energy transfer processes make noticeable changes in the composition of the analyzed area in XPS.



Figure 60 - Region degradation rate from GO5 irradiated by x-rays in XPS. The complete decay and growth of each region follows an exponential fit, however the initial change best follows a second order polynomial fit.

Because all O/C, R1 or R2 values are compared as a ratio to the respective starting percentage for the specific component for various radiation sources and exposure times, a new naming scheme will be used. The naming scheme will follow the form X_{ab}, where 'X' is

the component ratio being measured (O/C, R1 or R2), 'a' is the radiation source (x = x-ray, γ = gamma radiation, Ar = Argon ion, α = alpha, and n = neutron), and 'b' is the exposure time (i=initial, f = final, or a number_hr/s = specific exposure time in either hours, hr, or seconds, s).

3.3.2.1 Gamma Irradiation

The in-situ radionuclide Co-60 source had a very low D_{AR} , which was 9 orders of magnitude smaller than the x-ray source in the XPS. Therefore, it was important to limit the x-ray exposure during XPS measurements to an absolute minimum without losing too much information from the analyzed spectra. The GO material was irradiated by the in-situ gamma source for 3.5 hrs, and the total absorbed dose from gamma irradiation was 0.1 Gy. The XPS measurement parameters were similar to those for the x-ray irradiation study but the dwell time of the spectra was reduced to 300 ms. Therefore the total x-ray exposure time for each C 1s and O 1s spectra measurement was 170 seconds and $O/C_{x150_s} = 0.999$. The measured O/C_{vf} was 0.998, which is not statistically significant. It is clear that very little oxygen removal occurs as a result of the gamma irradiation.



Figure 61 – The change in R1, R2, and R3 for GO after a 3.5 hr γ-irradiation

Although no oxygen is removed during irradiation, a significant change in the species does occur. It is unexpected to see such a large change in the R1, R2, and R3 composition after the γ -irradiation because the total energy absorbed was 0.1 Gy. The total energy absorbed from x-rays during the XPS measurement of the γ -irradiated sample was 1.2 MGy, a difference of 7 orders of magnitude. Yet, as shown in Figure 60, the change in the R1, R2, and R3 composition after 170 seconds of x-ray exposure (1.2 MGy absorbed) is nearly zero. The Compton scattering effect from the 1.25 MeV gamma photons is negligible compared to the x-ray photons (1486 eV), however pair production is possible. The pair production attenuation coefficient is quite small (4.92E-3 g/cm²), but pair production is enhanced if a material is significantly hydrated.⁸⁵ It is possible that the GO material is still hydrated even in the ultra-high vacuum load lock chamber (1E-7 Torr). This is shown by both the oxygen 1s spectra from XPS (Figure 52b) and the oxygen k-edge absorption spectra from XANES (Figure 57).

The transition from R2 oxygen species to R3 (carboxylic acid) is most likely a result of an intermediate interaction between water and the absorbed gamma photon. Water radiolysis results in both reducing radicals (e_{aq} and H) and oxidizing products (OH, HO₂, and H₂O₂).⁸⁵ These radicals from water can form as a result of the high energy photoelectrons from x-ray irradiation, but become more prominent in gamma and charged particle radiation (alpha and Ar+ ion). ⁸⁵ Additionally, radiation sources with high absorbed dose rates (10⁷Gy s-1) often cause water to form more molecular products (H2 and H2O2) than radicals because of interradical interactions along each particle track leading to the formation of a molecular product.⁸⁵

Another reason there is a more noticeable change in composition after this small absorbed dosage of gamma radiation is related to the setup for this in-situ study, because the GO surface that is analyzed is opposite the side of the radionuclide gamma source. The particle track of the gamma photon through the 10 μ m GO interacts with the material via photoelectric absorption and pair production, both of which often result in the formation of free radicals or electrons. As the gamma beam attenuates through the GO this cascade of electrons spreads and energy is transferred over a larger area (Figure 62). Therefore, both the presence of water and the attenuation of gamma particles through the GO could be the cause for the increased change in composition.



Figure 62 - Monte Carlos analysis of gamma particle interaction in GO. The tracks show the path of generated electrons as a result of a flux of 1E7 gamma photons and the color indicates the total energy deposited as a result of the generated electron.

3.3.2.2 Alpha Irradiation

The GO material was irradiated by a Po-210 alpha source for 14.5 hrs, with an additional xray exposure time was 670 seconds. The $O/C_{x670_s} = 0.997$, which is exceeded by the measured change from the alpha irradiation $O/C\alpha f = 0.985$. The change in the O/C as a result of the alpha irradiation is shown in Figure 63. After 14.5 hrs of alpha irradiation the total absorbed dose was 0.16 Gy. It is unknown whether the limit for the $O/C\alpha f$ is truly 0.988 times the initial $O/C\alpha i$ value, because the photon flux from the radionuclide is very low. Higher flux alpha sources are available but would require more elaborate setup to analyze in-situ. The trends in composition change are similar to the gamma irradiation study, however the total change is greater, relative to the absorbed dose.



Figure 63 - In-situ XPS measurements of alpha irradiated GO sample, comparing the change in O/C (a) and the regions of C 1s (b) as a function of alpha irradiation time.

One reason why there is a greater change in composition as a function of absorbed dose is that the attenuation of alpha particles through matter is much greater than any of the previously analyzed radiation sources. All alpha particles are completely absorbed in GO after traveling through 27 μ m of material. The average energy deposition as a function of distance (or linear energy transfer, LET) is 2.5 E-1 dMeV/dµm, however as the alpha particle attenuates through the GO it loses velocity and the energy deposition increases

(Figure 64). The thickness of the GO was tailored to the depth where the greatest amount of energy is transferred. This is likely why a greater change is seen for the alpha particles at lower total absorbed dose quantities.



Figure 64 - Energy loss as a function of attenuation distance for a Po-210 alpha particle in GO. The alpha particle is completely absorbed after traveling through 27 μm of GO. As the particle cascades through the material the particle slows down, increasing the interaction time as well as the amount of energy transferred per distance traveled. This information was acquired from running simulation using SRIM (stopping range for ions in matter).

3.3.2.3 Neutron Interaction

The interaction mechanisms of a neutron particle in GO is not well known and therefore the attenuation coefficient and energy absorption coefficient were not defined. It was determined that the total absorption of GO was negligible during the transmission analysis. The variance in the neutron beam flux was greater than any change seen when the 20 μ m GO material obstructed the beam path. The average, minimum, and maximum neutron transmission is compared to the measured transmission for the GO material after the 1 minute exposure in Table 24. Because the difference in transmission was negligible, the total absorbed dose could not be determined.

Measurement	Neutron Transmission –	
	Raw Counts (n/cm2/sec)	
Unobstructed Beam	2.58 <u>+</u> 0.12 E9	
GO 16	2.59 E9	

Table 23 - Neutron beam transmission measurement for GO16 was measured at the Breazeale Nuclear reactor. The GO material was 20 µm thick and the total exposure time was 1 min.

The total x-ray exposure time for the XPS measurements of GO pre-neutron irradiation and GO post-neutron irradiation was 446 seconds, which yields a O/C_{x446_s} =0.998. Both the GO16 control sample and the GO16 neutron radiated sample are shown in Figure 65 with the x-ray corrected value. The moderate change in O/C for the GO16 control sample gives further proof for the need of in-situ measurements when studying the chemistry of GO. The difference in the O/C change between the control sample and the neutron irradiated sample is 0.012. However it is unknown if this change seen for the neutron irradiated material is statistically significant, because only one control sample was measured. Further analysis of the neutron irradiation is needed to provide the degradation rate as a function of energy absorbed.


Figure 65 - XPS measurement of the O/C ratio for GO after thermal neutron irradiation and a control sample. Because measurements could not be performed in-situ using the XPS, the material had to be transported to the Breazeale reactor. The two samples (GO16 neutron and GO16 control) were transported in vacuum sealed bags and UV impenetrable carrying case. Because the neutron beam exposure could not be performed under high vacuum, the control sample was removed from the sealed container for the same duration as the irradiated GO sample to determine how GO chemistry was altered by the environmental conditions at the reactor.

3.4 Discussion and Conclusion

A detailed analysis of the x-ray interaction with GO revealed the order in which oxygen functional groups are removed and the rate of removal for those species that are photodissociated. The absorption cross section for the photodissociated species (carbonyl and epoxide groups) are also calculated from the XEOL measurements. This is important for the research of GO because x-ray techniques are often used to analyze the chemistry, structure, and electronic structure. The work here has provided the degradation rate for GO in typical x-ray technique environments, which can be used to determine the maximum allowable x-ray exposure before significant changes in the GO chemistry begin to take place. An initial investigation of the mechanisms involved during the radiolysis of GO have also revealed that intercalated water is likely a key component during the reduction process. Additionally, we have shown that when GO is irradiated by high energy radiation it has a luminescent peak in the optical region. Although the intensity of the luminescent peak is very low and requires the use of a micro-channel plate detector (in the XEOL system), the origin of the luminescent peak has been determined (carbonyl and epoxy species). Therefore, it may be possible to tailor the intensity of the luminescent peak by increasing the coverage of these species in GO. It has also been demonstrated that the luminescent peak does not shift as the material is reduced (O/C goes down), which is not the case for optically excited (UV and visible light) GO. This suggests that the mechanisms involved for the luminescence process as a function of high energy radiation are different than the mechanisms that induce luminescence as a function of optically excited GO. Furthermore, the controlled reduction of GO via high energy radiation allows for the O/C ratio to be tuned with an accuracy of 0.001 and unlike hydrazine reduction, which is also a slow reduction process, there are no additional constituents added to the system, for example nitrogen.

Lastly, the importance of in-situ measurements for GO is also made clear, due to the altered chemistry of control samples. Even when caution was used to isolate the GO control sample from potential reducing environments, a change in chemistry was still observed.

CHAPTER 4 – CONCLUSIONS AND FUTURE WORK

4.1 IMPACT OF RESULTS

Controlling the properties of the meta-stable GO is accomplished by tailoring the chemistry and structure of the material. By performing a comprehensive analysis of multiple synthesis parameters this work has identified which steps are most influential for the oxidation of the graphite. It was previously considered that the addition of the acid slurry/GO mix into the hydrogen peroxide/water solution halted the oxidation process, however it has been shown that there is a significant increase in the O/C ratio of GO as a result of the cleaning procedure. Additionally, this thesis proposes that the crystallite size of the starting graphite powder has the greatest impact on the subsequent GO flake size. The identification of these impactful synthesis parameters provides future GO research a means to control the physical and chemical structure. However, it is clear that the GO chemical structure is meta-stable, which was also shown in previous work.⁸ In order to investigate the interaction mechanism of a species with GO, it is essential that the system is isolated from any potential reducing environment. Not doing so would most likely result in a convolution of interacting species and render identification of the desired reaction to be complex.

The use of in-situ measurements is one way to overcome interaction with undesired reducing environments. The work here is the first known investigation of high energy irradiation of GO in-situ. The results have revealed the species that are targeted during high energy radiation as well as the rates at which decomposition occurs. These results directly impact any future GO research that utilizes x-ray techniques to analyze the chemistry of the material. If future opto-electronic applications of GO require the system to be exposed to higher energy irradiation, the degradation rates calculated here could be used as a guideline for the expected change in chemistry. Additionally, one desirable property of GO for the opto-electronic field is the ability to tune the O/C ratio, which in effect changes the photoluminescence peak.¹⁵ Each of the high energy radiation sources have a O/C reducing limit and the rate of change is dependent on the particle flux. Therefore, this would provide future opto-electronic GO research with a means to control the O/C ratio.

4.2 FUTURE WORK

4.2.1 Structure

Further investigation of the nucleation process is required to confirm the conclusion that oxidation is initiated at the crystallite edges. It is possible that increasing this crystallite size may also provide additional control over the total amount of oxygen functional groups formed on the GO. Previous work has shown that mild oxidation of GO still yields single layer flake material.¹¹³ Limiting the amount of oxygen functional groups present in the GO material and increasing the size of the GO flake could result in a transition to larger area pristine graphene during mild reduction processes. However, current reduction methods that completely remove the oxygen from GO are not mild and result in the generation of

defects and voids in the structure.²² The change in the physical structure of GO was not monitored as a result of the high energy irradiation. Future work could investigate the effect that high energy radiation has on the GO structure. Although it does not completely remove the oxygen from GO, it may be applicable as a complimentary reduction technique.

4.2.2 High Energy Interaction & Heterogeneous Material System

This thesis demonstrated that GO has luminescence as a result of high energy irradiation. The origin of the luminescent peak is related to the concentration of carbonyl and epoxy functional groups, however it is possible that other contributing mechanisms affect this peak. If the intensity of this luminescent peak could be enhanced it is possible that this material could be used as a non-electronic sensor for high energy radiation. Because there is no peak shift as a function of the dose of the high energy radiation it would strictly be used as a means of identification. It is unknown if the luminescent peak continues to red shift as the energy of the incident radiation is increased. If so, the GO material could be used to identify different types of radiation. There are already devices that can identify the energy of incident radiation as well as their doses,¹⁰¹ but GO may be able to be used as a continous permanent monitoring material system. Other research has shown that GO is compatible with polymers and paints and therefore could be applied to whatever to surfaces in the area where high energy radiation monitoring is desired.⁸³

However, one radiation type that was not proven to be absorbed by GO was neutron particles. It is possible that the addition of boron-10, an isotope of boron that decomposes when exposed to slow neutrons, could enhance the neutron sensitivity for GO. When boron-10 decomposes after neutron irradiation it produces a charged lithium ion, a gamma ray and an alpha particle (Figure 66). ¹¹⁴ Boron-10 exists naturally in all boron species, including hexagonal boron nitride (hBN).¹⁰¹



Figure 66 - The decomposition species of boron-10 after neutron absorption.¹¹⁴

Because hBN has nearly the exact same structure as graphite the two material systems are highly compatible.¹¹⁵ The compatibility of GO with hBN had not been shown previously, so it was explored. SEM of the hetero-material revealed that the smaller particles of hBN stack between the GO flakes (Figure 67). The presence of the hBN particles in the GO paper were confirmed through Auger analysis (Figure 68).



Figure 67 - GO paper with hBN particles packed between GO sheets. The splitting seen in (a) and the magnified image (b) show that hBN particles are present throughout many layers of GO.



Figure 68 - Auger electron spectroscopy is used to identify that the smaller particles in the GO matrix are hBN

When the heterogenous material, or BCON (boron-oxygen-carbon-nitrogen), was exposed to neutron radiation the transmission went down as compared to GO, but was still not statistically significant (Table 24). But because any neutron particles absorbed by the boron-10 species decompose to form alpha particles, it is expected that the interaction with GO would increase. The total attenuation length of the boron generated alpha particle in GO is 5 μ m. Thicker BCON paper material (20-30 μ m) was synthesized for this neutron irradiation. Further research is required to determine if a luminescent peak is generated during the neutron irradiation.

Table 24 – Neutron transmission measurements for BCON are compared against GO and unobstructedneutron beam.

Measurement	Neutron Transmission –		
	Raw Counts (n/cm2/sec)		
Unobstructed Beam	2.58 <u>+</u> 0.12 E9		
GO 16	2.59 E9		
BCON	2.58 E9		

This heterogeneous material was synthesized by sonicating hBN powder down to few layer material and then sonicating the few layer material into a GO suspension. It was found that the BCON suspension was pH dependent. At lower pH values, the hBN particles agglomerated and formed sheets of hBN (diameter up to few centimeters) that were orders of magnitude greater than the hBN flake size (~70 nm), as shown in Figure 69. This agglomeration suggests that the BCON material is a pH dependent amphiphile. However, further analysis is required to confirm this belief.



pH=3.5 pH=4.5

Figure 69 - BCON suspensions are pH dependent, at lower pH values the hBN agglomerates out of suspension. The suspensions shown have the same concentration of GO and hBN.

XPS results show that during this synthesis process, new chemical bonds are formed between the hBN material and GO sheets (Figure 70), most likely at defect sites of the GO material. It is unknown how this could affect the luminescent properties of this material as a function of radiation. Further analysis is required to completely understand this material system and how it interacts with high energy radiation.



Figure 70 - XPS analysis of BCON shows two unexpected peaks that represent a change in chemistry during the synthesis of the material.

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APPENDIX A - XRD MONOCHROMATOR COMPARISON

The graphite powders measured in XRD were measured with and without a diffraction monochromator installed. Each of the measurements are shown below, highlighting the varying degrees of cyrstallinity in each material. The spectra shown in red is the XRD measurement performed without a monochromator and the measurements shown in black are done with a diffraction monochromator.



Figure 71 - XRD of NF50 with monocrhomator (black) and without (red) with the blue lines indicating the diffraction plane peaks for graphite samples. The peaks present in the measured material are labeled.



Figure 72 - XRD of NF500 with monochromator (black) and without (red) with the blue lines indicating the diffraction plane peaks for graphite samples. The peaks present in the measured material are labeled.



Figure 73 -XRD of EG with monochromator (black) and without (red) with the blue lines indicating the diffraction plane peaks for graphite samples. The peaks present in the measured material are labeled.



Figure 74 - XRD of SG with monochromator (black) and without (red) with the blue lines indicating the diffraction plane peaks for graphite samples. The peaks present in the measured material are labeled.

Both the NF50 and SG, Figure 71 & 74, spectra show all the representative crystal planes of graphite. The {001} peaks for the natural flake graphite material are so intense that other lines are showing from the tungsten filament diffracting through the material. The use of the monochromator removes several of these lines from the spectra but not all, and the location of the expected peaks from the tungsten filament and the Cu-K-beta x-ray source are calculated through the following procedure for the diffraction peaks for each graphite:

Bragg's Law:	$n\lambda = 2dsin heta$	(X)
Source is Cu-K-alpha	$\lambda = 1.542 \left[\text{\AA} \right]$	

These calculations allow us to determine which peaks in the scan are due to instrumental effects and which may be a result of the graphite crystalline structure.

Table 25 - Calculated 2- θ value for varying radiation sources and diffraction planes of graphite. Those calculated peaks that match the peaks present in the XRD scans for graphite materials are highlighted in bold and red numbers.

Radiation	λ (Å)	2-θ	2-θ	2-θ	2-θ	2-θ	2-θ
Source		d(001)	d(002)	d(100)	d(101)	d(102)	d(103)
W-L-alpha 1	1.477	12.5	25.4	40.0	42.2	47.6	56.1
W-L-alpha 2	1.488	12.6	25.6	40.3	42.6	48.1	56.7
W-L-beta 1	1.282	10.9	21.9	33.9	35.6	39.9	46.1
W-L-beta 2	1.245	10.5	21.2	32.8	34.5	38.5	44.4
W-L-gamma	1.099	9.3	18.6	28.5	30.0	33.3	38.1
1							
W-L-gamma	1.062	9.0	18.0	27.5	28.9	32.1	36.6
3							
Cu-K-alpha	1.392	11.8	23.9	37.2	39.3	44.1	51.4

Bold #'s: diffraction lines that still show up with the monochromator **Red #'s:** diffraction lines that removed by the monochromator

The spectra for each graphite material shows a broad hump around the (001) peak, which is related to the presence of multiple scattering peaks resulting from the variety of radiation emitted from the tungsten filament. When the monochromator is used these lines are removed and only the (001) peak is present, shown as the peak values highlighted in red in Table 25. The (002) peak is representative of the layer spacing while the (001) peak is representative of the layer spacing while the (001) peak is representative of the graphite unit cell. The presence of these multiple scattering peaks when scanned without the monochromator is a characteristic of highly crystalline material. The NF50 material has the greatest number of additional peaks from these tungsten radiation species.

APPENDIX B - FT-IR OF EXPANDED GRAPHITE

The signal for the expanded graphite material was too small to identify individual peaks, therefore a baseline correction had to be performed. The following image is the before and after spectra for the EG from the Diamond-ATR.



Figure 75 - A baseline correction was performed for the EG sample and this figure shows the before and after IR spectra.

APPENDIX C - UNSUCCESSFUL RUNS

The powders used for GO-7 were mixed into the acid solution while the beaker was in an ice bath, yet the temperature exceeded 20°C (T – powder = 25°C), which caused excessive bubbling to occur. The final product for GO-7 was dark green. The cleaning procedure for other GO runs that started with 3 g of graphite took 2-4 weeks, therefore it was determined that it was not worth the effort to run the cleaning procedure for this material.

The run for GO-13 ended in a small eruption of powder during the water addition. The reason for this eruption is not clear, but is believed to be a result from insufficient cleaning of the beaker that was used for previous runs. This beaker had a layer of film around the upper half, which may have been a result of the N₂O₄ and N₂O₂ out-gassing during the acid/powder mixing step from previous runs. The phosphoric acid was never added to the sulfuric acid before mixing the powders during GO-15, which caused the exothermic reaction to reach 150°C and purple gas began effervescing. The purple gas was a result of the intermediate formation, dimanganeseheptoxide (Mn₂O₇), sparking and out-gassing.

APPENDIX D - XRD FULL SCAN OF GO MATERIALS

The following figures show the full XRD scan for each GO material that was measured through XRD. The blue lines in the survey scan represent the location of expected graphite peaks, which would show up if the material was not completely oxidized.



Figure 76 - Full XRD scan for GO4 showing (001) peak at 10.29° and the (100) peak at 42.20°.



Figure 77 - Full XRD scan for GO5 showing the (001) peak at 10.00°.



Figure 78 - Full XRD scan for GO6 showing (001) peak at 7.66°.



Figure 79 - Full XRD scan for GO9 showing (001) peak at 10.19°.



Figure 80 - Full XRD scan for GO10 showing (001) peak at 9.43°.



Figure 81 - Full XRD scan of GO11 with (001) peak at 10.86° and (002) peak at 26.45° and an unknown shoulder at 21.33°.



Figure 82 - Full XRD scan of GO12 showing (001) peak at 9.94°.

The GO samples with the greatest presence of graphitic peaks in descending order are GO11, GO4 and GO9 (Figure 81, 76, and 79 respectively). The inter layer spacing for each of these materials is as follows: GO11 is 8.14 Å, GO4 is 8.59 Å, and GO9 is 8.67 Å. Therefore we see that the amount of oxidized carbon is closely tied to the interlayer spacing of each GO material. The GO6 material, which was synthesized from NF500, also shows the greatest level crystallinity because the tungsten lines show up in the spectra.

APPENDIX E - CLEANING EFFECT DETAILS

All runs prior to run #6 were cleaned using the filtration method. Run #5 was cleaned through a hybrid filtration/centrifugation method. The GO from run #5 was filtered out of the acid slurry using the fritted filter and water was added as mentioned in the experimental section. However, after 4 days this water did not pull through the fritted filter and the GO material was poured into the centrifuge test tubes. This material was then run at 4000rpm for 30min to separate the GO from water. Then 30ml of HCl (5%) was added to each test tube of material (~1 g of hydrated GO material) and centrifuged at the same rate. This was the final step in the cleaning procedure and the material was then put into water and methanol:water (9:1) suspensions.

APPENDIX F – SEM PARTICLE SIZE ANALYSIS

Samples G010 and G011 were spun at higher rates to spread out the flake distribution so individual flake sizes could be measured. Because the GO particles were spread so far out with a spacing of 10-100 µm it was not feasible to analyze the particle size through AFM. Therefore SEM images were taken and it was assumed that particles seen in the micrograph were individual flakes. Using ImageJ the area of each identified GO particle could be measured. The figure below is an example of the SEM micrograph and the particles analyzed using ImageJ. It is likely that some particles are multiple flakes agglomerated together. It was too difficult to distinguish between individual particles using SEM because the contrast is very low. Therefore, it is assumed that the particle size analysis may even be an overestimate of the actual particle size. This would further support the conclusion that the starting graphite flake size is less impactful than the crystallite size on the subsequent GO flake size.



Figure 83 - SEM and ImageJ analysis of GO10 to determine individual flake area distribution

APPENDIX G - GO THIN FILM THICKNESS CONTROL



Figure 84 - AFM section analysis shows varying GO thin film thicknesses of 4 nm (a), 6 nm (b), 19nm (c), and 60nm (d). The scan profile above each AFM image shows the points where the vertical distance measurement was made.

APPENDIX H – OUTLIERS FROM FIGURE 52

The outlier measurements at ~220 MGy and ~370 MGy are most likely related to a slight change in the height of the sample bar. The following graph shows that the intensity for both the carbon and oxygen 1s peaks increase at ~200 MGy, levels off to a constant reduction rate, then drops at ~370 MGy (Figure 52). The irradiation measurement was paused at these points in the run to check on the condition of other samples on the sample mount bar. Although the stage position is saved in the XPS it is possible that the height position was not exactly identical to the previous position. Any change in the height greater than 0.5 μ m can lead to a change in the relative intensity.



Figure 85 - Peak area for the carbon 1s and oxygen 1s spectra as a function of absorbed radiation.

APPENDIX I – XPS PEAK FITTING

Many fitting models were performed for each GO sample analyzed during the in-situ XPS measurements. Because peak fitting in XPS is so robust, nearly any spectra can be manipulated inaccurately if the user is unaware of the necessary constraints and essential parameters for each peak fit. Firstly, it is rare for XPS peak FWHM to vary more than ± 0.2 eV for each peak fitted within one photoelectron region (aka carbon 1s photoelectron region).⁶⁵ Secondly, increasing the number of peak fits for one photoelectron region will generally reduce the standard deviation of the fitting, therefore it is beneficial if there is prior knowledge of the species present in the material. Knowing which species are present will allow one to put constraints on the peak parameters, such as the position, FWHM, peak shape, and/or intensity. Some peak positions are slightly outside of the pre-determined range for the carbon species, specifically the C-OH & C-O-C peak region because only one peak is representing both species.

Model #	Remaining 0%	RSD	ΔFWHM (eV)
1	5.2	7.6	0.55
2	-2.4	7.9	0.28
3	-0.8	2.8	0.55
4	-1.8	3.7	0.65
5	1.5	7.8	0.35
6	1.4	9.6	0.28
7	1.4	6.9	0.4
8	-0.4	9.1	0.25
9	0.5	6.5	0.3
10	-1.1	9.8	0.3
11	-2.3	8.3	0.2

Table 26 - GO5 x-ray irradiation (4 MGy) XPS component peak fitting analysis

Model #	Remaining 0%	RSD	ΔFWHM (eV)
1	2.1	4.6	0.20
2	2.1	3.9	0.40
3	3.9	5.7	0.27
4	2.4	4.4	0.20
5	2.3	4.4	0.76
6	1.9	3.8	1.06
7	2.1	3.7	0.49
8	-1.8	3.9	0.49
9	-2.4	4.9	0.13
10	0.6	5.4	0.16
11	0.6	5.1	0.21

 Table 27 - G05 x-ray irradiation (637 MGy) XPS component peak fitting analysis



Figure 86 - Peak positions for the analyzed peaks in (a) GO5_A and (b) GO5_B