GRAPHENE BASED NANO-COATINGS: SYNTHESIS AND PHYSICAL-CHEMICAL INVESTIGATIONS

By

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DECLARATION

I hereby declare that "Graphene based nano-coatings: Synthesis and physical-chemical investigations" is my own work, that it has not been submitted or part of it for any degree of examination at other university, and that all sources I have used or quoted have been indicated and acknowledged by means of complete references.



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Philippians 4 vs.13, I can do all things through CHRIST who strengthens me.

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''Longer is the wait, higher is the reward'' 'There is light at the end of every tunnel''



DEDICATION

This thesis is dedicated to my late grandmother Mrs. Manjiyela Amelia Nyangiwe who has supported me with her pension grant, given me years of joy and happiness. She believed in me and before she passed 7 years ago, she asked me to bring home a car with a wheel at the back.



ABSTRACT

It is well known that a lead pencil is made of graphite, a naturally form of carbon, this is important but not very exciting. The exciting part is that graphite contains stacked layers of graphene and each and every layer is one atom thick. Scientists believed that these graphene layers could not be isolated from graphite because they were thought to be thermodynamically unstable on their own and taking them out from the parent graphite crystal will lead them to collapse and not forming a layer.

The question arose, how thin one could make graphite. Two scientists from University of Manchester answered this question by peeling layers from a graphite crystal by using sticky tape and then rubbing them onto a silicon dioxide surface. They managed to isolate just one atom thick layer from graphite for the first time using a method called micromechanical cleavage or scotch tape.

In this thesis chemical method also known as Hummers method has been used to fabricate graphene oxide (GO) and reduced graphene oxide. GO was synthesized through the oxidation of graphite to graphene oxide in the presence of concentrated sulphuric acid, hydrochloric acid and potassium permanganate. A strong reducing agent known as hydrazine hydrate has also been used to reduce GO to rGO by removing oxygen functional groups, but unfortunately not all oxygen functional groups have been removed, that is why the final product is named rGO.

GO and rGO solutions were then deposited on silicon substrates separately. Several characterization techniques in this work have been used to investigate the optical properties, the morphology, crystallography and vibrational properties of GO and rGO.

The main reason for using Hummer's method in this work is because out of all methods of fabricating graphene, it is another low-cost and a very promising method for large scale production of graphene or reduced graphene oxide.

The second part of this thesis is about reducing GO using the sun and artificial light, GO solutions were exposed to the sun and artificial light for 2h, 4h, 8h and 16h. Three characterization techniques i.e XRD, UV-VIS and ATR-FTIR were used to study the crystallographic and optical properties of rGO.



OD	zero-dimensional
1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
CNT's	Carbon nanotubes
ITO	Indium Tin Oxide
TEM	Transmission Electron Microscopy
MWCNTs	Multi-Walled Carbon Nanotubes
SWCNTs	Single-Walled Carbon Nanotubes
C-C	Carbon-Carbon bond
SLG	Single-Layer Graphene
SiO ₂	Silicon Dioxide
FET	Field Effect Transistor
NEMS	Nano Electromechanical System
HOPG	Highly Oriented Pyrolytic Graphite
Si	Silicon
SiC	Silicon Carbide
CVD	Chemical Vapor Deposition
GO	Graphene Oxide
AFM	Atomic Force Microscopy
SEM	Scanning Electron Microscopy
LABS	Laboratory for Accelerator Based Sciences
MRD	Materials Research Department
XRD	X-Ray Diffraction
r-GO	reduced Graphene Oxide
ATR-FTIR	Attenuated Total Reflectance Fourier Transform Infrared

UV-Vis	Ultra-Violet and Visible
UWC	University of the Western Cape
H_2SO_4	Sulphuric acid
KMnO ₄	Potassium Permanganate
H_2O_2	Hydrogen Peroxide
HCI	Hydrochloric acid
iLO	in-plane longitudinal optic
LO	longitudinal optic
OFG	Oxygen Functional Groups



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CHAPTER 1 : INTRODUCTION TO GRAPHENE

1.1 Introduction

Graphene is a flat monolayer of carbon atoms tightly packed into a twodimensional (2D) honeycomb lattice. It is the basic building block for graphitic materials of all other dimensionalities as shown in figure 1.1.

Graphene has unique physical, chemical and mechanical properties [1,2]. It is the first known two-dimensional material which has a singular band structure whereby the valence band and conduction band are touching each other [1].

Graphene is mostly encounted in nature in the form of graphite, which is merely a stack of graphene layers held together by Van der Waals interactions [1].

Graphene attracted a lot of interest in the research community [3,4] due to its potential for applications in electrochemical devices, heat insulation, and also as a transparent and flexible semiconductor, where it can replace the rather expensive indium tin oxide (ITO) [5-7]. It is theoretically the hardest material ever due to the sp² carbon-carbon bond configuration [1].

Graphene has a high electron mobility and electrons can travel freely through it for long distances without being deviated [8]. This makes graphene a very appealing material for fast transistors [8].

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Figure. 1.1: Graphene the building block of all graphitic forms, it can be wrapped into a 0-D (buckyballs), 1-D (nanotubes) and stacked to form the 3-D (graphite) [1].

1.2 BRIEF HISTORY OF GRAPHENE

In 1947 scientists predicted graphene to have perculiar properties like, very high intrinsic Young Modulus [9], high thermal conductivity [10] and high electron mobility [1].

Due to the above listed properties, graphene can have many technological applications. Figure 1.2 shows a model of graphene which was presumed not to exist as a free standing material, due to the thermodynamic instability [11].

Two scientists, Landau and Peierls first started the debate that 2D materials were thermodynamically unstable and thus could not exist [13]. Their debate pointed out that an anomalous contribution of thermal alterations in low-dimensional crystal lattices should lead to the removal of atoms that become equivalent to interatomic distances at any finite temperature [14].

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Later this debate was extended by Mermin, and was substantially endorsed by many experimental observations [15]. As the melting temperature of thin films expeditiously decreases with decreasing thickness of stacks of atomic layers [16]. With the above mentioned arguments 2D materials were postulated not to exist until 2004.

In 2004 two scientists from the University of Manchester, Andre Geim and Kostantin Novoselov used a very novel approach to isolate graphene from graphite for the very first time. They managed to extract single atom thick graphene from graphite by pilling off graphene layers from graphite and transferred them onto a thin silicon dioxide substrate.

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They used a method called micromechanical cleavage or scotch tape method to isolate graphene from graphite Figure 1.3 shows atomic force microscopy image of graphene on top of an oxidized Si substrate. On October 5, 2010, the Nobel Prize in Physics for the year was awarded to Andre Geim and Konstantin Novoselov for their work on graphene [8].



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Figure. 1.2: A model of graphene structure [14].



Figure. 1.3: Atomic force microscopy image of a graphene crystal on top of an oxidized Si substrate [17].

1.3 AIM AND OBJECTIVES OF THE PROJECT

The first objective of this project is to synthesize graphene using Hummer's method, then deposit graphene solutions onto a silicon dioxide substrate in order to investigate its physical and chemical properties using various characterization techniques.

The second objective of this thesis is to synthesize graphene by light irradiation of graphene oxide nano-flakes.

1.4 THESIS OUTLINE

Chapter 1: This chapter is mostly about introduction of graphene, it gives a clear explanation of what is graphene. Later it traces back to a brief history of graphene and also mentions recent (2010) Noble Prize in graphene. The chapter also describes the method used for the first isolation of graphene. Lastly this chapter talks about the main purpose of this thesis.

Chapter 2: This chapter is about carbon based materials, it describes in depth graphite, diamond, carbon nanotubes, fullerenes and graphene and its prominent properties.

The last part of this chapter is all about synthesis methods of graphene, it describes in details various methods of producing graphene, which include Hummer's method.

Chapter 3: Various techniques that have been employed in this project are discussed, later this chapter explains in depth the experimental procedure

that has been used to synthesis graphene oxide (GO) and reduced graphene oxide (rGO).

Chapter 4: This chapter is the core chapter for this project because that's where the obtained results are discussed in details. All the obtained micrographs and acquired data will be interpreted and discussed. This chapter will be wrapped up by a brief conclusion of the entire work.

The last part in this chapter is about the second objective of this project, irradiation results of GO using sunlight and artificial light have been discussed.



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CHAPTER 2: OVERVIEW OF CARBON BASED MATERIALS

2.1 Introduction

As stated in chapter 1, graphene is the mother board of all graphitic materials. This chapter focuses on various carbon based materials that can be derived from graphene in details. It starts by explaining single wall carbon nanotubes (SWCNTs) and their brief history, then after it describes multi wall carbon nanotubes (MWCNTs), diamond and graphite and their properties are summarized in appendix A and B.

2.2 CARBON NANOTUBES



Carbon nanotubes were discovered by Iijima in 1991 as a byproduct of the arc discharge synthesis of C_{60} . The carbon nanotubes were observed as multi-wall tubes nesting in a concentric way [1]. These multi-walled carbon nanotubes (MWCNTs) are composed of 2 to 50 coaxial graphitic carbon sheets with a smallest inner diameter of around 2 nm and length up to 1 µm. Figure 2.1 shows high resolution transmission electron microscope (HRTEM) images of the MWCNTs.

Carbon nanotubes can be categorized as single-walled nanotubes (SWNTs) and multi-walled nanotubes (MWNTs) depending upon the number of walls [2]. The main difference between SWNTs and MWNTs is that, SWNTs contain only one rolled graphene layer whereas MWNTs contain two or more concentric layers [1].

In 1993 Iijima and Bethune discovered single-walled carbon nanotubes (SWCNTs) [3,4]. Single-walled nanotubes are generally more compressed than the multi-walled tubes, with diameters typically in the range of 1 nm to 2 nm. Figure 2.2 displays how SWCNTs consist of a single sheet of a honeycomb network of carbon atoms, called graphene that is rolled up ceaselessly into a tubular form [1].

SWCNTs can be electrically semiconducting or metallic depending upon their diameters and chirality, these stem from their dominant properties originating from its one-dimensionality. These important physical properties were later proved experimentally in different electrical and optical measurements [6].

It was postulated that a piece of SWCNT can be a transistor and this was demonstrated by Iijima [6]. There are many other applications that demonstrate the unique properties of carbon nanotubes, like the electron emitter source with high current density, the probe needle for scanning probe microscopes, highly conductive electrical wire, gas absorbers' high thermal conductor for the heat radiator and molecular sieves [1].

These properties have attracted a lot of interest of many research scientists both academic and industrial arena [7-9]. This is because of their promising applications in nanotechnology.

Another more general difference between carbon nanotubes and conventional crystalline materials is their increased surface area, that is to say they have more atoms on their surface in a given area [1].

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MWCNTs consist of multiple rolled layers of graphene. The interlayer distance in MWCNTs is close to the distance between graphene layers in graphite, approximately 3.4 Å [2]. Figure 2.3 shows a MWCNT model in 3-D.

MWCNTs are composed of many concentric graphene layers; their diameters can range from 10 to 50 nm while their length is more than 10 μ m [11]. MWCNTs can be thought of as concentric single walled nanotubes of increasing diameter arranged in a rounded fashion [12].



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Figure. 2.1: High resolution TEM images of MWCNTs showing different diameter and diverse number of graphene sheets [1].



Figure. 2.2: Rolling of graphene into a SWCNT [5].



Figure. 2.3: A model of multi wall carbon nanotube MWNT [10].

2.3 GRAPHITE

Graphite is a very well known allotrope of carbon and the most abundantly occurring from all allotropes of carbon. It is has a crystalline structure made up of sheets of carbon atoms bonded in a 2-dimensional space and stacked on top of one another by weak van der Waals forces. These 2-dimensional carbon-carbon bonded (C-C) structured sheets are known as graphene, hence graphite can be viewed as sheets of graphene stacked on top of one another [13]. Each carbon in graphite is sp³-hybridized as shown in figure 2.4 below.

The most common stacking sequence of the graphite crystal is hexagonal (alpha) with an ABCABC stacking order, in other words the carbon atoms in every other layer are superimposed over each other as shown in figure 2.4. The stacking of these layers occurs in two slightly different ways i.e. hexagonal and rhombohedral.

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The spacing between the layers is relatively large (0.335 nm), or more than twice the spacing between atoms within the basal plane and approximately twice the van der Waals radius of carbon. The carbon atoms within a graphite layer form a regular hexagonal network with a C-C distance of 1.421 Å [14]. Within each layer a carbon atom is bonded to three other carbons, forming a series of continuous hexagons in what can be considered as an essentially infinite two-dimensional molecule.

The stiffness of graphite along the plane is very large due to strong σ bonds in the horizontal plane direction, it is very weak perpendicular to the planes because of the weak van der Waal's force. The planes can be easily divided to make graphite a soft material [15]. Graphite is an electrical conductor and it is chemically reactive. It has a different crystal structure from diamond. It is soft and grey to black in color. Various properties of graphite are summarized in appendix A [13].

2.4 DIAMOND

Diamond is an allotrope of carbon, the atoms are arranged in a variation of the face-centered cubic (FCC) crystal structure and also tetrahedrally bonded carbon atoms. All bonds between the carbon atoms (σ -bonds) emanate from sp³ hybrid atomic orbital. It has lattice constant of 3.56 Å and the distance between the atoms is 1.54 Å as shown in figure 2.5 [16].

Diamond has many applications in industry because of its excellent physical properties which are generally originating from strong covalent bonds between its atoms. It has been used as drilling and polishing tool [17]. The most important characteristics of diamond are its hardness, thermal conductivity, wide band gap and high optical dispersion [18]. The various properties of diamond are summarized in appendix B [13].



Figure. 2.4: Crystal structure of graphite showing (ABCABC) stacking sequence [14].


Figure. 2.5: crystal structure of diamond with its lattice parameters [16].

2.5 FULLERENES

The term fullerene is too broad, it covers a collection of hollow cages of carbon atoms interlinking pentagons and hexagons [19]. Fullerenes, a new form of carbon were discovered in 1985 [20]. The discovery of C_{60} carbon cage molecules popularly known as fullerene, named after the famous Architect, Buckminster Fullerene, opened new and large vistas in understanding these molecules [21]. Fullerenes have many applications including sensors, catalysts, superconductors, optical and electronic devices, polymers composite and high energy fuels [1,23,24,25].

Buckminsterfullerene is a pure carbon molecule that consists of at least 60 atoms of carbon and has a buckyball structure as shown in Figure 2.6.

Fullerenes are very hard molecules, able to resist high pressures. The physical strength of fullerene does offer potential in nanotechnology however like nanotubes they do not bond to each other chemically, they rather stick together through much weaker van der Waals forces, the very same forces that keep layers of graphene in graphite together [19].

2.6 GRAPHENE

Graphene is a purely carbon-carbon 2D material with a honeycomb structure, a one atom thick layer of carbon atoms sheet bonded to one another by sp² hybridization [25]. The monolayer nature of graphene has been verified using Raman spectroscopy [26]. From Raman spectroscopy results, 2D band comes from the second order resonant Raman scattering zone boundary phonons and it does not represent any defects. The

appearance of 2D peak confirms that GO has been reduced to rGO. Figure 2.7 show schematics of carbon allotropes of different dimensionalities.



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Figure. 2.6: A model of C₆₀ Buckminsterfullerene [25].



Figure. 2.7: Graphitic materials 3D: sp³–bonded diamond (left) and graphite which consists of stacked layers of 2D graphene sheets. 1D: nanotubes can be imagined as rolled up graphene, while 0D: Buckminster fullerenes (buckyballs) represent wrapped graphene sheets [27].

2.6.1 PROPERTIES OF GRAPHENE

2.6.1.1 MECHANICAL PROPERTIES

The sp² carbon-carbon bond is theoretically the existing strongest bond, making graphene the hardest possible material [28]. There are necessary elastic parameters required to define mechanical properties of a material like the Young modulus the stiffness of the material, the Poisson's ratio, and the shear modulus. The shear modulus and Poisson's ratio have not been confirmed experimental on monolayer sheets so far [29]. It has been shown in the literature that graphene is mechanically very strong and it has a breaking strength 200 times than steel, a bulk strength of 130 GPa [30]. Graphene's spring constant is different from the one of bulk graphite, ranging from 1-5 N/m and a Young modulus is approximately 0.5 TPa [30].

2.6.1.2 ELECTRONIC PROPERTIES SITY of the WESTERN CAPE

Graphene is a near perfect electronic conductor because it is a zero band gap semiconductor hence the conduction and valence bands overlap as shown in figure 2.8 [32]. The electrons momentum k is linearly related to the energy E near the edges of the 2D first Brillouin zone and the electrons behave like mass less Dirac fermions [32].

It has a very high electron mobility, this has been proven both theoretically and experimentally. Charge carries in graphene can travel ballistically over submicron distances because it displays a very high electronic quality [31]. Transport measurements show that graphene has an electron mobility of approximately 15, 000 cm² V⁻¹ s⁻¹ at room temperature [31]. Electron mobility is just an indicator of the speed of electrons in a solid. The use of materials with high electron mobility gives the possibility to realize high speed transistors and 20 000 cm^2/Vs was reported for single-layer graphene (SLG) at low temperatures [32-35].

2.6.1.3 THERMAL PROPERTIES

Thermal conductivity of graphene is dominated by phonons and has been measured to be approximately 5000 $Wm^{-1}K^{-1}$ [36]. The thermal conductivity of graphene is much greater compared to the values of 300 W/mK and 3500 W/mK for MWCNT and SWCNT respectively. The non-contact optical technique was used to measure the thermal conductivity of graphene. These carbon allotropes exhibit higher thermal conductivities.

2.6.1.4 OPTICAL PROPERTIES

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Graphene has a very high optical transparency which means that it can be a good transparent conducting electrode [37], it has high opacity for an atomic layer [38]. The optical transmittance (T) and reflectance (R) which are

$T = (1 + 1/2\pi a)^{-2}$	equation 1
and	

R =	1/4n ² a ²	equ	ation	2
-----	----------------------------------	-----	-------	---

where

$a = 2\pi e^2 / hc \approx 1/137$	equation 3
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e is the electron charge, c the light speed, and h Planck's constant) gives an opacity of approximately 2.3% which is given by

 $(1 - T) \approx \pi a$equation 4

Dirac fermions in graphene have frequency conductivity which is approximately to

 $\square e^2/2 h$ equation 5

From the infrared through the visible range of the spectrum [39,40]. The definition of T and R in terms of theoretical constants that do not directly involve material parameters is stated to be a result of the structure and electronic properties of graphene [41]. Figure 2.9 shows the transmission of graphene.

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Figure. 2.8: A representation of the electronic band structure of graphene [32].



Figure. 2.9: (a) graphene absorbs about 2.3% of white light and the small insert demonstrate the sample design, also line scan profile shows the intensity of transmitted light [42,43].

2.6.2 POSSIBLE APPLICATIONS OF GRAPHENE

Graphene has many potential applications due to the above mentioned unusual properties but it is still in its infant stages. Graphene can make good sensors due its 2D honeycomb structure. The most attractive application field for graphene is high-speed transistors because of its high-mobility and many research efforts have been put into it. Due to its high electronic quality, graphene has also enthralled the interest of technologists who see it as a way of constructing ballistic transistors. Graphene has a high carrier mobility, as well as low noise, allowing it to be used as the channel in a field effect transistor (FET). Graphene films are currently examined for metallization lines in devices [44], high speed devices associated high mobility of the carriers, and several other applications including spintronics [45] and sensors [46,47].

2.7 METHODS OF SYNTHESIZING GRAPHENE

2.7.1 Introduction

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Several methods of preparing graphene have been discussed in this section, starting with micromechanical exfoliation also known as the scotch tape method, this is a 2010 Noble Prize winning method in physics. It is a very easy method for isolating graphene from graphite but has its limitations.

The second method discussed is the epitaxial growth from silicon carbide (SiC), in this method SiC is heated at high temperatures under vacuum to produce graphene.

The third method is a chemical vapor veposition (CVD) in which substrates like Copper or Nickel are being used as catalysts, these substrates are then placed into a furnace and heated at low vacuum to 1100 °C.

Lastly a chemical method also known as the Hummer's method is also described, this is the main method used in this thesis for the synthesis of graphene oxide and reduced graphene oxide. This process is about oxidizing graphite flakes into graphene oxide in the presence of sulphuric acid, hydrochloric acid and potassium permanganate, then graphene oxide is later reduced by a strong reducing agent known as hydrazine hydrate.

2.7.2 MECHANICAL EXFOLIATION

Mechanical exfoliation is one of the methods used to isolate graphene. It uses adhesive tape to exfoliate patterned, highly oriented pyrolytic graphite (HOPG) as shown in figure 2.10.

The tape is then folded several times to obtain few layered graphene sheets. The more you fold the more flakes split. At the end the thin flakes are attached to the film that can be transferred to a suitable substrate like silicon oxide, as depicted in figure 2.11 [49].

Mechanical exfoliation is the simplest way to prepare micro-size graphene flakes for fundamental research purposes [50]. The advantage of this method is that, it can produce large size and unmodified graphene sheets. Its disadvantage is the very small scale of production [51]. Andre Geim and Konstantin Novoselov used this method to isolate graphene for the very first time in 2004 [48].



Figure. 2.10: Mechanical exfoliation of graphene using Scotch tape from HOPG [48].



Figure. 2.11: (a) deposition of tape exfoliated graphene flakes over Si/SiO₂ substrate (b) an example of a graphene monolayer under optical microscope [49].

2.7.3 EPITAXIAL GRAPHENE GROWTH

Graphene can also be obtained by simply heating silicon carbide (SiC) to very high temperatures (1200 °C) in vacuum [52]. When a SiC sample is heated under vacuum, silicon atoms sublimate from the substrate. The dismissal of Si leaves surface carbon atoms to rearrange themselves into graphene layers. The thickness of graphene layers depends on the annealing time and temperature [53]. This method relies on the graphitization of SiC by thermal decomposition [54]. The epitaxial graphene grown on the Si substrate shows the most promise with excellent crystal quality and large coverage. However similar to the chemical vapor deposition (CVD) technique, more work still needs to be done on obtaining further control of the graphene film thickness and grain boundaries.

2.7.4 CHEMICAL VAPOR DEPOSITION

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The chemical vapor deposition (CVD) can be used as a process of thermal deposition of hydrocarbons onto transition metals substrates. CVD is currently one of the promising methods for mass production of high quality graphene. This method uses a metal substrate such as copper or nickel as catalyst, the metal substrate is put into a furnace and heated at a low vacuum to around 1100 $^{\circ}$ C, then the heat anneals the substrate there by increasing its domain size [55].

Methane and hydrogen are then flowed through the furnace, the hydrogen acts as a catalyst between a reaction of methane and the surface of the metal substrate, this causes the atoms of carbon to be deposited onto the surface of the metal through chemical adsorption, this process is depicted in figure 2.12 [56]



Figure. 2.12: A schematic depiction of graphene deposition on copper substrate using CVD technique [57].

2.7.5 CHEMICAL EXFOLIATION

Chemical exfoliation method involves intercalating molecules in bulk graphite by chemical treatment in order to separate the crystalline planes into individual graphene layers [58]. This method makes use of an intermediate step in which graphite is chemically modified to make it water dispersible. One way to achieve this is to oxidize graphite to graphite oxide which can be intercalated with water to separate the graphene layers as demonstrated in figure 2.13.



Figure. 2.13: Molecular model for the conversion of graphite to chemically derived graphene through oxidation and reduction processes [59].

Chemical conversion of graphite to graphene oxide (GO) has emerged to be a viable route to graphene based sheets in considerable quantities [60-64]. Graphite oxide (GO) is usually synthesized through the oxidation of graphite using oxidants including concentrated sulphuric acid, hydrochloric acid and potassium permanganate based on Hummers method [65]. Compared to pristine graphene, GO is heavily oxygenated bearing hydroxyl and epoxy groups on sp³ hybridized carbon on the basal plane, in addition to carbonyl and carboxyl groups located at the sheet edges on sp² hybridized carbon [66].

GO is highly hydrophilic and readily exfoliates in water, yielding stable dispersion consisting mostly of simple layered sheets GO. It is important to note that although graphite oxide and GO share similarities (i.e. surface functional group), their structures are different. Graphene is a monolayer material produced by the exfoliation of GO. It is very difficult to get 100% pure graphene without oxygen functional groups. After reducing graphene oxide by using a strong reducing agent called hydrazine hydrate, the final product is named reduced graphene oxide (rGO) because not all oxygen functional groups have been removed.

All the chemical balanced equations for the processing of GO from graphite are summarized in Appendix C.

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CHAPTER 3: CHARACTERIZATION TECHNIQUES

3.1 ATOMIC FORCE MICROSCOPY

3.1.1 Introduction

Atomic force microscopy (AFM) is a technique that is broadly used to characterize materials on the nanometer scale. It is a type of scanning probe microscopy (SPM) in which a sharp tip is scanned across the sample to obtain information about the surface morphology. The information acquired from the interaction between the tip and the sample's surface can reveal physical topography of the specimen. The sample's physical properties can also be determined by the AFM through different working modes [1].

3.1.2 Instrumentation

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The morphology of the specimen can be determined from the interaction between the surface and the tip of the cantilever. This type of interaction is related to the motion of the cantilever which is measured by a light lever method. In this method, a laser beam is directed to the backside of the cantilever near the sharp tip and reflected onto a photon detector. The laser beam will then be reflected to different spots of the photon detector when the cantilever bends, thus the photon detector can monitor the motion of the cantilever. Figure 3.1 below shows schematic diagram of the instrument[1].



Figure 3.1: Schematic diagram of an instrument [2].

3.1.3 Imaging modes in AFM

AFM can be operated in three different modes, contact-mode, non-contact mode and tapping-mode. When a scan is done in contact mode, a constant force is applied to the surface of the sample, following the topography of the surface as it is scanning. This results in the cantilever deflection due to topography. The surface morphology of the specimen can be mapped out by the feedback information from the system control of the cantilever deflection.

In a non contact mode long range forces of interaction such as magnetic dipole and electrostatic forces can be measured. This can be achieved by scanning across the sample while holding the sharp tip at 10 to 100 nm above the sample surface. Dynamic mode can be used in conjunction with the non contact mode and can be varied by using a piezo driver, and this can be used to vibrate the cantilever while scanning across the sample.

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In the tapping mode, the cantilever keeps vibrating when the tip is scanning across the surface, while the signal is being measured at every point when the tip is down on the surface. When the vibrating cantilever comes close to the surface, the amplitude and phase of the vibrating cantilever may change. These changes in the amplitude and phase are recorded because they are related to the topography applied of the surface [1].

The main purpose of using AFM in this work is to determine the morphology and roughness of graphene oxide and reduced graphene oxide on a uniform substrate. Figure 3.2 shows typical AFM images of graphene oxide and reduced graphene oxide. The red spots in figure 3.2 demonstrate the distance where the thinkness was measured.



Figure. 3.2: Images of confined graphene oxide and reduced graphene sheets. (a) AFM image of graphene oxide sheets on freshly cleaved mica, demonstrating a single graphene oxide sheet, (b) AFM image of a reduced graphene oxide on freshly cleaved mica sonication [3].

3. 2. X-RAY DIFFRACTION

3.2.1 Introduction

X-ray diffraction (XRD) is a characterization technique used for the investigation of microstructural properties of materials. X-rays are scattered when interacting with the atoms of the material being investigated, the diffracted X-rays helps in revealing the atomic structure of the material studied. This technique has its origin in von Laue's discovery in 1912 [4].

3.2.2 Instrumentation

Using X-ray diffraction, crystallographic and elemental structure of a specimen can be determined. In this technique, X-rays of known wavelength are passed through the specimen and diffracted by the atoms of the sample. Those X-rays that have constructive interference after being diffracted off the atoms give a unique diffraction pattern of the lattice in the crystal that is being investigated.

The best way to describe diffraction of X-rays is to use the famous Bragg's law, which says the incident X-rays strike the planes of the crystal with an incident angle θ and after that a diffraction peak is formed when the Bragg condition is fulfilled:

 $2d \sin\theta = n\lambda$equation 6

Where λ represent the wavelength, d is the distance between each adjacent crystal planes, θ is the Bragg angle where diffraction peak is observed and n is the integer number and is named the order of refraction [5]. Figure 4.3 shows a schematic diagram of X-ray diffraction. X-ray diffraction has been

used in this work to study the crystallography of graphene oxide and reduced graphene oxide.



Figure. 3.3: displays, the incident X-rays and reflected X-rays resulting to an angle of θ symmetric to the normal of crystal plane [5].

3.3. SCANNING ELECTRON MICROSCOPY

3.3.1 Introduction

The scanning electron microscope (SEM) is a technique that images the sample surface by scanning it with a high energy beam of electrons in a raster scan pattern. This technique renders a large depth of field, which means the area of the sample that can be viewed in focus at the same time is enlarged [6].

3.3.2 Instrumentation

The electrons interact with the atoms of a sample, producing signals that comprise information about the sample's surface topography, composition and other properties.

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The electrons are generated by thermionic emission of tungsten element under high electric potential, and are centered by the Wehnelt Cylinder when they pass though the aperture. The electrons are accelerated down the column by a high electric potential. These electrons then pass through a series of magnetic lenses. The diameter of the electron beam is reduced by condenser lenses to produce smaller spot and then finally this beam of electrons is focused on the sample using the objective lens [7].

When the electrons in the SEM machine interact with the specimen, three signals are produced i.e. secondary electrons, back scattered electrons and characteristic X-rays. In the primary detection mode and secondary electron imaging, the SEM can produce very high-resolution images of a sample surface. SEM micrographs have a large depth of focus and can render

images showing three-dimensional features that can be useful in understanding the structure of a sample.

X-rays are released when the electron beam excites an inner electron shell of a sample, promoting it to higher energy shell resulting in a vacancy. When a higher energy electron falls off to fill the vacancy in the inner shell, it gives off its energy in a form of X-rays. These characteristic x-rays are used to identify the elemental composition of the sample [7]. Figure 3.4 shows a schematic diagram of SEM.





Figure. 3.4: Schematic diagram of SEM [14].

3.4 TRASMISSION ELECTRON MICROSCOPY

3.4.1 Introduction

Transmission electron microscopy (TEM) is a microscopy technique whereby a beam of electrons is transmitted through a thin specimen, the transmitted electrons then hit a fluorescence screen whereby the image of the specimen is revealed.

TEM is capable of imaging at a significantly higher resolution than light microscope, owing to the small de Broglie wavelength of electrons. This inherent property of electrons makes it possible to study features of the sample that are at the nanometer scale.

TEM is frequently used to image nano-sized materials to the atomic scale resolution, where a transmitted electron beam passes through the ultra thin sample to the imaging lenses and the detector. As graphene oxide (GO) and reduced graphene oxide (rGO) are atomic thick layers, a good resolution can be obtained at low operational voltage.

Recently few researchers have used a new class of TEM which is an aberration corrected in combination with monochromator that can provide 1 Å resolution at an acceleration voltage of only 80 kV [8,9].

Meyer's group showed for the very first time direct high resolution images of the graphene lattice depicting every single carbon atom arranged in hexagonal way [10].

3.4.2 How does TEM work

When an accelerated beam of electrons entrenches upon a sample a valuable variety of interactions takes place (figure.3.5).

The interactions that happen during the collision of the electron beam and the sample include the following; transmitted electrons, backscattered electrons, secondary electrons, coherent elastic scattered electrons, incoherent inelastic electrons, incoherent elastic forward scattered electrons, characteristic, and continuum X-rays, Auger electrons, long-wavelength radiation in the visible, ultraviolet, and infrared regions of the spectrum, lattice vibrations(phonons), electron oscillations in metals (plasmons), electron-hole pair generation and electrical current [11].

A beam of electrons are centered on a single, pinpoint spot or element on the sample being investigated. The electrons then combine with the sample and only those that go past unhampered hit the phosphor screen on the other side. Then electrons are converted to light and an image is assembled. The dark parts of the image correspond to parts on the specimen where fewer electrons were able to go through (either absorbed or scattered upon impact) [12].

The lenses in a TEM are different from lenses in a conventional microscope, these are actually EM devices that can center the electron beam to the desired wavelength or size [12].



Figure. 3.5: displays variety of interactions take place when a beam of electrons entrenches upon a sample [11].

3.5 ATTENUATED TOTAL REFLECTANCE FOURIER TRANSFORM INFRARED SPECROSCOPY (ATR-FTIR)

3.5.1 Introduction

An attenuated total reflection (ATR) system is used to analyze liquids and solid samples, it functions by measuring the change in a totally internal reflected infrared beam. When an infrared beam comes in contact with a sample an evanescent wave extends beyond the surface of the crystal into the sample held in contact with the crystal as indicated in Figure 3.5 below



Figure. 3.6: shows a multiple reflection ATR system [13].

3.5.2 Brief theory of ATR-FTIR

The theory of ATR-FTIR system dates back to the work of two scientists Jacques Fahrenfort and N.J Harric. These two scientists initiated and suggested a broad range of applications. They described the evanescent wave and how it is related to the concept of internal reflection [13].

The concept of internal reflection spectroscopy arise from the fact that electromagnetic radiation travelling in an optically dense medium of refractive index n_1 undergoes total internal total internal reflection at an interface of an adjacent medium of lower optical density (refractive index n_2 < n_1). This wave is called evanescent [14]. The above phenomenon happens only when the angle of incidence exceeds a critical angle θ_c demonstrated by Snell's law:

 $Sin_{\theta c} = \frac{n^2}{n^1} \dots \dots equation 7$

Using ATR-FTIR oxygen containing groups like carbonyl, carboxylic acid, hydroxyl and epoxides can be determined and also can be indexed.

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3.6 ULTRA-VIOLET TO VISIBLE LIGHT (UV-Vis) SPECTROSCOPY

3.6.1 Introduction

UV-Vis spectroscopy and IR spectroscopy covers different regions of the spectrum and study different phenomena, the first studies electronic transitions in an optical medium while the second deals with molecular vibration and rotational modes.

Each distinctive absorption coincides to an electronic transition [15,16]. Using the Beer's Law

A = εbc.....equation 8

one can determine absorbance or concentration where

- A = absorbance
- ϵ = molar extinction coefficient
- b = path length
- c = concentration

3.6.2 How does UV-Vis spectroscopy work

In this technique (UV-Vis), a sample is probed with photons of wavelength in the range of ultraviolet to visible. When this photon increases with the electron structure of the sample, the photons are absorbed depending on the electronic arrangement of the sample. The absorbance plot of the UV-Vis can be used to determine optical properties of the sample.UV-Vis spectroscopy can be used to analyze solutions of transition metal ions, organic compounds with a high degree of conjugation, or those with alternating single and multiple bonds, and charge transfer complexes [17].

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3.7 RAMAN SPECTROSCOPY

3.7.1 Introduction

Raman spectroscopy is an analytical technique that employs the principle of inelastic scattering of monochromatic light. This technique can be used in studying the vibrational modes of the molecules in the samples.

In an inelastic scattering the frequency of photons of a monochromatic light alters against interaction with a sample. Photons of the laser light are being reflected by the sample and then reemitted. The frequency of the reemitted
photons is shifted up or down in comparison with original monochromatic frequency, which is called the Raman shift. This shift is very important because it tells the information about vibrational, rotational and other low frequency transitions in molecules. Solid, liquid and gaseous samples can be analyses using Raman spectroscopy [18].

Raman spectroscopy uses only a single frequency of radiation to irradiate the sample and it is the radiation scattered from the molecule, one vibrational unit of energy different from the incident beam, it does not need matching of the incident radiation to the energy difference between the ground and excited states [19].

In graphene and in other carbon-based materials, resonance Raman takes place when the incident photons' energy matches that of electronicvibrational transitions [20]. The main purpose of using Raman spectroscopy in this project is to characterize graphene and graphene oxide layers, in terms of the number of layers present and presence of defects [2].

3.7.2 Basic theory of Raman spectroscopy

When light interacts with matter, the photons which build up the light may be absorbed or scattered or may not interact with the material and may proceed straight through it. When the energy of an incident photon corresponds to the energy gap between the ground state of a molecule and an excited state, the photon may be absorbed and the molecule promoted to the higher energy excited state [19]. It is this adjustment which is measured in absorption spectroscopy by the detection of the loss of that energy of radiation from the light. it is also possible for the photon to interact with the molecule and scatter from it.

In this scenario there is no need for the photon to have an energy which corresponds the difference between two energy levels of the molecule. The scattered photons can be observed by collecting light at an angle to the incident light beam, and provided there is no absorption from any electronic transitions which have similar energies to that of the incident light, the efficiency increases as the fourth power of the frequency of the incident light [19].

3.7.3 Raman Fundamentals

The scattering of monochromatic radiation that is incident on a sample can reveal information of the sample's molecular structure. If the frequency of the scattered radiation is analyzed, not only is the incident radiation wavelength observed via elastic scattering but also a relatively small amount of radiation is scattered inelastically at some different wavelengths, referred to as Stokes and anti-Stokes Raman scattering. Figure 3.7 displays the schematic diagram of Raman scattering principle.



The scattered light is inelastically scattered Raman. The scattered radiation occurs in all directions and may also have observable changes in its polarization along with its wavelength.

It is the shift in wavelength of the inelastically scattered radiation that provides the chemical and structural information. Raman shifted photons can be of either higher or lower energy, depending upon the vibrational state of the molecule under study. A simplified energy diagram that illustrates these concepts is shown in figure 3.8.



Figure. 3.8: simplified energy diagram.



Stokes radiation happens at lower energy (than the Rayleigh radiation, and anti-Stokes radiation has greater energy. The energy increase or decrease is associated to the vibrational energy levels in the ground electronic state of the molecule and the observed Raman [19].

Shift of the Stokes and anti-Stokes features are a direct measure of the vibrational energies of the molecule. Figure 3.9 displays schematic diagram of Stokes and Anti-Stokes.



Figure. 3.9: illustration of the stokes and anti-stokes Raman spectrum.



The energy of the scattered radiation is lower than the incident radiation for the Stokes line and the energy of the scattered radiation is higher than the incident radiation for the anti-Stokes line.

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The energy increase or decrease from the excitation is related to the vibrational energy spacing in the ground electronic state of the molecule and the wavenumber of the Stokes and anti-Stokes lines are a direct measure of the vibrational energies of the molecule [19].

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CHAPTER 4: RESULTS AND DISCUSSION

4.1. EXPERIMENTAL PROCEDURE

4.1.1 Hummers method

Out of all the four methods of preparing graphene discussed in chapter two, Hummers method was used in this project because it has a great potential for the mass production of graphene. All the reagents used in the synthesis were of analytical grade and no further purification was performed on them [1].

2 grams of natural flake graphite power were added to 46 ml of concentrated H_2SO_4 at 0 °C, this was followed by 6 grams of KMnO₄ which was added gradually while stirring and cooling the mixture in an ice bath. The mixture was then stirred at 37 °C for 3 hours, then 92 ml of distilled water was slowly added to the mixture and the temperature of the solution was maintained below 90 °C for 30 minutes. After that 280 ml of 30% H_2O_2 solution was added to the mixture, and the mixture was subsequently stirred for 12 hours.

A brown-yellowish solution was observed and the solution was then sonicated for 30 minutes at 35 °C, the product was filtered and the residue was washed with 500 ml of 10% HCl aqueous solution to remove metal ions, this was followed by a thorough rinse with distilled water, the resulting solution was a graphene oxide (GO). 1 ml of hydrazine hydrate was added to the solution and stirred for 6 hours at 40 °C, this was done to remove oxygen from the graphene oxide (GO). Since it is difficult to completely

remove all the oxygen the GO, the resulting solution is called reduced graphene oxide (rGO) [2].

All the reagents chemical equations used in the Hummer's method are listed in the appendix C. Figure 4.1 below shows GO solution before and after addition of hydrazine hydrate. The brownish GO solution changed to black which means that graphene oxide was successfully reduced to graphene.



Figure. 4.1: prepared solutions of graphene oxide (GO) and reduced graphene oxide (rGO).

4.1.2 Sample preparation

Silicon wafers were used as substrates of choice for the deposition of both graphene oxide and reduced graphene oxide. Two silicon wafers were cut into a square of 1cm × 1cm using a diamond scribe, after that wafers were broken by hand at the scratch. They were cleaned by sonication process in ethanol for 10 minutes. Solutions of graphene oxide and reduced graphene oxide were sonicated for 15 minutes. After 15 minutes the solutions were deposited drop wise to the entire surface of two separate silicon wafer substrates using a pipette.

They were left for 2 hours to dry. Then the GO and rGO deposited on silicon substrates were analyzed using various analytical techniques.

4.2 Experimental Results

4.2.1 Introduction

The techniques used to characterize graphene oxide (GO) and reduced graphene oxide (rGO) films are atomic force microscopy (AFM), scanning electron microscopy (SEM), transmission electron microscopy (TEM), x-ray diffraction (XRD), ultra-violet to visible (UV-Vis) spectroscopy, ATR-FTIR and Raman spectroscopy. All these techniques confirmed a successful synthesis of GO and rGO.

4.3 OPTICAL PROPERTIES

4.3.1 Attenuated Total Reflection Fourier Transform Infrared (ATR-FTIR) Spectroscopy

ATR-FTIR is a nondestructive technique for finding the chemical composition of materials from their chemical bonding. It can be used as a qualitative tool to characterize materials from the molecular vibrations of the chemical bonds in the sampling volume.

ATR-FTIR spectra were recorded on a Perkim Elmer Spectrum 100 spectrometer in the 4000-500 cm⁻¹ range at the University of the Western Cape, South Africa. **Figure 4.2** below depicts the obtained ATR-FTIR spectra of GO and rGO.

From the spectra in figure 4.2 various oxygen functional groups on GO were observed, a peak at 3560 cm⁻¹ on a GO sample was observed which is due to the O-H stretching vibrations, another peak at 1810 cm⁻¹ was also observed and is due to stretching vibrations of the C=O bonds. A small peak at 1480 cm⁻¹ was observed and is believed to emanate from the skeletal vibrations from unoxidized graphitic domains [3].

The observed oxygen functional groups on the GO sample confirms the oxidation of the graphite to GO as expected from the chemical reactions shown in appendix C.

In the case of ATR-FTIR spectrum of rGO as shown in figure 4.2, a peak at 3440 cm⁻¹ was observed which is due to the O-H stretching vibrations and the same peak also confirms the reduction of rGO to deoxygenation. Another peak at 1540 cm⁻¹ was also noticed and is a stretching vibrations of C=O [4]. The two peaks at 950 cm⁻¹ and 650 cm⁻¹ are due to stretching vibrations of C-O and C-H respectively. Since it is difficult to completely reduce GO to pure graphene, it is expected to have small traces of oxygen functional groups in the sample, as it is evident from the peaks at 1540 cm⁻¹,3440 cm⁻¹ and 950 cm⁻¹. It is worth mentioning that these oxygen functional groups have been significantly reduced due to the reduction process.



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4.3.2 Ultraviolet-Visible (UV-Vis) Spectroscopy

The UV-Vis spectra of the samples were recorded on a CECIL 2021, 2000 Series at iThemba LABS, South Africa. It was mainly used to further confirm the oxidation and reduction of GO and rGO.

The UV-Vis spectra in figure 4.3 reveal structural changes of GO before reduction and after it has been reduced to rGO. The GO absorption peak appeared at 225 nm confirming the oxidation of graphite to GO. After the reduction of GO the UV absorption shifted peak has undergone a redshift as seen from the plot in **figure 4.3**, this is due to the electron conjunction

within the sheets which were restructured upon the reduction of GO to rGO. These two prominent peaks are very similar to the ones reported in the literature [4].



Figure. 4.3: UV-Vis Spectra of GO and rGO.

4.4. rGO and GO MORPHOLOGY

4.4.1. Atomic Force Microscopy

The morphology of graphene oxide (GO) and reduced graphene oxide (rGO) deposited on silicon substrates were studied using the Nanoman V AFM in a tapping mode, at iThemba LABS, South Africa. Figure 4.4 shows AFM image of GO with a measured roughness of 3.571 nm.

Comparing GO and rGO coatings, GO sheets were observed to be tightly stacked than the rGO due to the presence of covalently bonded oxygen and the conversion of sp^3 hybridized carbon atoms to sp^2 [5].

The roughness of GO and rGO is about 3.571 nm and 3.373 nm respectively proving that the reduced graphene oxide has less stacked layers and a smoother surface compared to graphene oxide because more exfoliation took place [6].

The rGO film was also deposited on a silicon substrate and its AFM image is as shown in figure 4.5, the roughness of the coating was measured to be 3.373 nm.



Figure. 4.4: AFM image of graphene oxide with a roughness of 3.571 nm.



Figure. 4.5: AFM image of reduced graphene oxide with a roughness of 3.373 nm.

4.4.2 Scanning Electron Microscopy

SEM was used as a complimentary technique to the AFM to confirm the morphology of GO and rGO films. Structurally GO sheets are similar to the rGO sheets, the main difference is that GO sheets have oxygen containing functional groups such as epoxides, alcohols and carboxylic acids [7,8].

The SEM image of GO as shown in figure 4.6 (a) illustrates a typical folding of ripple patterns of chemically exfoliated GO.

From figure 4.6 (a), the GO image shows wrinkled patterns, which contrasts with the smooth structure of rGO in **figure 4.6** (b). It is hypothesized that this structural difference is due to the presence oxygen functional groups in the GO and the lack thereof in the rGO.

Comparing SEM images of rGO and GO head to head, rGO is more agglomerated and coalesced than GO because almost all of oxygen functional groups have been removed during chemical reduction process.



Figure. 4.6: SEM image of GO and rGO deposited on a silicon substrate.

4.4.3 Transmission Electron Microscopy

For further analysis of GO and rGO, FEI Tecnai GO-20 TEM operated at 200 kV using an energy filter of 20 eV was used. TEM samples were prepared by depositing GO and rGO on silicon substrates. Figure 4.7 (a)-(b) shows GO TEM images at different magnifications, the images show layered structures.

These layered GO TEM images have rough surfaces as determined from the AFM results. This roughness is due to the oxidation of the sheets.

The GO sheets in figure 4.7 (a)-(b) are tightly packed together hence having flake-like shapes, which means GO sheets were still not well exfoliated.

Figure 4.8 (a)-(b) also shows TEM images of rGO sheets which are stacked on top of one another to form a film.

Both rGO images at different magnifications demonstrate no ripple like arrangements from chemically exfoliation, single sheet of graphene can be clearly seen from the TEM micrographs.

These rGO TEM images are slightly transparent than the densely packed GO sheets which appear as flake like structures on top of each other as shown in figure 4.8(a)-(b). This is because the rGO sheets are more separated from one another due to the exfoliation and reduction processes.

rGO films are smoother than GO films, which suggest that after the addition of a very strong reducing agent plenty of oxygen functional groups have been successfully removed.



Figure. 4.7: (a) TEM GO image with a scale of 200 nm (b) TEM GO image with a scale of $0.5\mu m$.



Figure. 4.8: (a) TEM rGO image with a scale of 0.2 μ m (b) TEM rGO image with a scale of 20 nm.

4.5. CRYSTALLOGRAPHY

4.5.1. X-ray Diffraction

The microstructural properties of GO and rGO were studied using X-ray diffraction (XRD) technique, this was carried out using a Brucker D8 advance GER, x-ray diffractometer using Copper K_a irradiation (wavelength = 1.5406 Å). The operating voltage and current were 40 kV and 300 mA respectively at iThemba LABS, South Africa.

The XRD patterns of GO and rGO exhibits diffraction peaks at 11.4° and 26° respectively as shown in figure 4.9 below.

The d-spacing of the interlayers of GO and rGO as calculated by Bragg's Law are 7.3 Å for GO and 3.5 Å for rGO.

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GO displays a very strong Bragg peak at $2\theta = 11.4^{\circ}$ which corresponds to an interlayer spacing of about 7.3 Å demonstrating the presence of oxygen functionalities. GO was reduced to graphene as evidence by the appearance of the (002) Bragg peak centered at $2\theta = 26^{\circ}$ which corresponds to an interlayer spacing of about 3.5Å.

After the chemical reduction the hydrophilicity of the water dispersed GO sheets gradually decreased, leading to an irreversible agglomeration of rGO sheets [10,11].



Figure. 4.9: the XRD plot of GO and rGO.

4.6 VIBRATIONAL PROPERTIES

4.6.1 Raman spectroscopy

So far Raman spectroscopy is the most accurate and trusted technique to characterize GO and rGO. Figure 4.10 shows Raman spectrum of graphene oxide.

From figure 4.10, the G band was observed at approximately 1595 cm⁻¹ which is due to the isolated double bonds that resonate at higher frequencies. This G band corresponds to the first-order scattering of the E_{2g} mode observed for sp² domains [12]. The D band was observed at approximately 1310 cm⁻¹ and it is ascribed to a breathing mode of k-point phonons of A_{1g} symmetry [13].

Raman spectrum of rGO in figure 4.11 below shows three very important peaks, D band at approximately 1350 cm⁻¹, G band at approximately 1580 cm⁻¹ and 2D band at approximately 2696 cm⁻¹.

From figure 4.11, the D band peak comes from a second-order process including one in plane transverse optic (iTO) phonon and a defect at the K-point. D band peak suggests that the formed rGO is disordered and has defects in it. The proposed defects may involve some vacancies and strained pentagon that result in the non-uniformity of the layers [14].

G band is a basic Raman characteristic appearing from the E_{2g} in-plane vibration at the Brillouin zone centre of the atoms. G peak is from the first-order Raman scattering process and it indicates the doubly degenerate in-plane longitudinal optic (iLO) phonon modes. At approximately 1630cm⁻¹

narrow G* band intensity peak appeared which is due to the double resonant Raman process, this G* band is like 2D band but it includes one longitudinal optic (LO) and in-plane longitudinal optic (ITO) phonon [14].

2D band comes from the second order resonant Raman scattering zone boundary phonons and it does not represent any defects. The appearance of 2D peak confirms that GO has been reduced to rGO.



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Figure. 4.11: Raman spectrum of rGO.

4.7 GRAPHENE SYNTHESIS BY LIGHT IRRADIATION OF GRAPHENE OXIDE NANO-FLAKES

4.7.1. Introduction and aim

It is universally known that the preparation of high quality graphene on a large scale and in a cost-effective manner is essential for many technological applications. Graphene oxide (GO) has emerged as the precursor of choice for bulk production of graphene-based materials, as it can be synthesized from inexpensive graphite powders.

Several techniques have been developed to reduce GO to graphene, including chemical reduction and thermal annealing. Recently, photo-reduction of GO has been carried out using flash reduction irradiation with a 663 nm continuous-wave (CW) laser as well as a 790 nm femto-second laser irradiation. Unfortunately, the effective reducing agents are generally toxic while the laser based photo-reduction techniques are expensive [15].

In this chapter, a simple method is described for reduction of GO solution by a free and green irradiation based technique. The majority of oxygencontaining functional groups of GO were removed by the sunlight irradiation and simple artificial light sources. This chapter intends to identify the effectiveness of the much wider than green on the artificial sun based photoinduced reduction of the GO solutions.

4.7.2. Chemical reduction of graphene oxide nano-sheets

As it is shared by various scientific disciplines, stretching from cosmology to material sciences, carbon and hydrogen are among the universal and basic elements of the Mendeleev periodic table. Carbon possesses various allotropics including diamond, graphitic carbon, carbon nanotubes, fullerenes, and the recently synthesized graphene. Graphene nanosheets are atomically thick, 2-D platelets exhibiting carbon atoms in hexagonal honeycomb arrangements [16]. These sp² hybridized atomic scaled sheets of carbon possess a substantial set of unique desirable properties. This latter singular set includes a large mechanical stiffness of about 1 TPa [17], a significant thermal conductivity of the order of 5×10^3 W/m⁻¹K⁻¹ [18] and an exceptional charge carrier mobility of the order of 25×10^4 cm²/V⁻¹s⁻¹ [19].

Consequently, graphene is being studied for various promising and potential use in a variety of physical-chemical applications that exploit these remarkable properties [20,21] ranging from gas sensors [22] to lithium-ion battery electrodes including the emerging graphene based transparent electrodes field [23,24].

As it is well established, the primary synthetic procedure for producing processable quantities of colloidal graphene, known also as highly reduced graphene oxide (HRGO) [25] entails the reduction of aqueous or organic dispersions of GO [26], a highly oxidized derivative of graphene possessing various oxygen-containing functional groups such as epoxy, hydroxyl, carbonyl, and carboxyl [27-29]. These groups, noticed on both the edge as well as on the basal plane of the nanosheets, acquaint sp³ defect sites to the nanosheets, distorting the intrinsic conjugated Π system and bringing down the overall strength and electrical conductivity [30].

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The reactivity of these groups creates graphene oxide nanosheets extremely attractive as building blocks for a wide range of macroscopic structures, as they can be readily functionalized and or modified with a variety of "surfactants" [31,32]. Current reduction methods for producing graphene nano-suspensions from graphene oxide typically afford nanosheets with high C/O ratios that exhibit good electrical conductivity, but are effectively inactive for chemical functionalization due to the low density of reactive groups remaining on the sheet surface. The main approach comprises the full exfoliation of GO into individual GO sheets followed by their in-situ reduction to produce individual graphene-like sheets.

More precisely, GO is synthesized by the oxidative treatment of graphite via one of three principal methods developed by Brodie [33], Hummers [34], and Staudenmeier [35]. It still keeps a layered structure, but is very lighter in color than graphite due to the loss of electronic conjugation brought about by the oxidation phase. Compared to HRGO sheets, and according to the most recent studies [36-41], GO comprises of oxidized graphene sheets having their basal planes decorated mostly with epoxide and hydroxyl groups, in addition to carbonyl and carboxyl groups located presumably at the edges (Lerf-Klinowski model). These oxygen functionalities provide the graphene oxide layers of GO hydrophilic and water molecules can readily intercalate into the interlayer galleries. GO can therefore be also considered of as a graphite-type intercalation compound with both covalently bound oxygen and non-covalently bound water between the carbon layers. Indeed, rapid heating of GO results in its expansion and delamination caused by rapid evaporation of the intercalated water and evolution of gases produced by thermal pyrolysis of the oxygen-containing functional groups [42].

Such thermal treatment has recently been proposed to be capable of making individual functionalized graphene sheets. GO is electrically insulating and thus cannot be used, without further processing, as a conductive nanomaterial [43,44]. Notably, it has been exhibited that the electrical conductivity of GO can be revived close to the level of graphite by chemical reduction [45]. The research of reductions of GO is still at an early stage. To that end, various chemical reductions of exfoliated graphene oxide sheets with several reducing agents were carried out and it was that found hydrazine hydrate ($H_2NNH_2-H_2O$) to be the best one in producing very thin graphene-like sheets, consistent with previous *Boehm et al reports* [46,47].

4.7.3 Light photo-induced reduction of graphene oxide nano-sheets

Given the worldwide interest in the large scale preparation of graphenebased materials [48-50], the international community set out to develop a general and reproducible approach for the preparation of graphene sheets from graphite at a mass scale and a competitive cost. Yet, this latter strategy is based on GO or HRGO as basic graphene precursors. The usage of light as a mean to reduce GO nano-flakes to graphene nano-sheets is an Indeed, laser attractive path. induced graphite oxide/graphene transformation in films was confirmed by Liu et al [51], Sokolov et al [52], and Zhang et al [53]. In addition, Trusovas et al [54] have recently demonstrated the direct local formation of few layers of graphene by direct laser writing on thin films of graphene oxide in the pico-regime.

More precisely, with a standard NdYAG irradiation of a fluence varying between 0.01 to 0.3 J/cm² and a repetition rate of about 100 kHz in air, the resistance of the GO decreases by 4 to 5 orders of magnitude. By

conducting additional experiments in nitrogen and argon atmosphere, they achieved a material with higher I_{2G}/I_D ratio as it has been shown by Raman spectroscopy. In the femto-regime, *Zhang et al* demonstrated the direct imprinting of micro-circuits of graphene on graphene oxide films by femtosecond laser reduction. More precisely, it was clearly evidenced that the surface height of the micro-patterns was lower than the rest of the film due to the loss of oxygen's as confirmed by XPS and XRD investigations. The corresponding electric resistivity and conductivity of as-reduced graphene were found to have a strong dependence on the output of the femtosecond laser source while the current-voltage of the synthesized graphene based micro-circuits showed typical linear relationship, indicating the stable conductivities. Overall, the laser irradiation reduction of graphene oxide might pave a way to graphene based nano-electronics.

In addition to IR laser reduction of GO in both femto and picosecond regimes as previously highlighted, Rao et al [55] extended the study to VIS and UV laser radiations based reduction. More specifically, effect of irradiation on graphene oxide by UV radiation based light and KrF excimer laser has been investigated. Both sunlight and ultraviolet light reduce graphene oxide well after prolonged irradiation, yet the KrF laser irradiation produces graphene with negligible oxygen functionalities within a relatively short time.

In this study, which is the background of our complementary studies, one should highlight the major parts of Rao's et al work [55]. The graphite oxide was prepared by the standard modified Hummer's method with graphite oxide readily forming a stable colloidal suspension in water. The aqueous suspension was subjected to ultrasonic treatment (300 W, 35 kHZ) to produce single-layer graphene oxide. The GO solution was taken in a petri dish it was exposed to sunlight for a few hours.

For treatment with ultraviolet radiation, the solution was irradiated with a Philips low-pressure mercury lamp (254 nm, 25 W, 90 μ W/cm²). A Lambda Physik KrF excimer laser (248 nm, 5 Hz) was employed to irradiate aqueous solutions of GO taken in a quartz vail. The aluminum metal slit acting as a beam shaper which usually gives a rectangular beam was removed during laser irradiation of the solution. This makes laser energy almost uniform throughout the area where graphene oxide is present. A 300 mJ beam energy at 5 Hz repeat-rate was used for the purpose. The reduced graphene samples obtained by irradiation with sunlight, ultraviolet light and KrF excimer laser will be S_{un}RGO, U_{UV}RGO and L_{aser}RGO respectively.

Apart from graphene oxide reduction by various irradiation sources, graphite oxide solution in water was directly irradiated with excimer laser for an hour to see whether sonication step can be avoided. In such experiments, the initial GO solution in water medium was brownish yellow in color. It gradually turned reddish after about 2h of irradiation by sunlight. It finally turned black in color after ~10 h of irradiation by sunlight. The color change of the graphene oxide from brownish yellow to black was a clear evidence of the occurrence of reduction phenomenon. From the IR spectra, it was observed that the intensity of the carbonyl stretching band decreased substantially after ~10 hour irradiation. Similarly, the intensities of bands due to other oxygen containing functional groups also decreased after the prolonged sunlight irradiation. More graphene edges were visible on the surface after irradiation. The most interesting results were obtained with KrF excimer laser treatment. The brownish yellow colour of the graphene oxide solution became deeper brownish red even after short laser irradiation (approximately 4 minutes of laser treatment, and about 1000 laser shots at 300 mJ). After ~1h of laser treatment i.e. about 18000 laser shots, the graphene oxide solution turned black in color. This fast color change

obtained with the excimer laser was related to the large laser fluence as compared to the areal energy density for sunlight and ultraviolet light. This concurred with the near disappearance of the carbonyl stretching band as well as of other bands due to oxygen functionalities after 1 h of irradiation in the IR spectrum.

Excimer laser irradiation not only reduced the graphene oxide effectively but also fragments the graphene. Solid graphene oxide required only 4-5 laser shots (1 second time for 5 Hz reprate) to be completely reduced to black graphene, devoid of any oxygen containing functional groups. Such reduction of graphene oxide in a few seconds makes excimer laser an excellent choice for reduction. UV (254 nm) mercury lamp used in Rao's et al experiment were 3 mW /cm² and 90 μ W/cm² respectively [55]. For pure comparison, the areal power density of KrF excimer laser was thus approximately ~33 times larger than that for the mercury lamp. X-ray photoelectron spectroscopy of solid graphene oxide and excimer laser reduced graphene oxide (LRGO) was also carried out and the signals of C 1s and O 1s were analyzed. It was found that the signals due to C=O and C-O at 286.5 eV and 285 eV were not observed in LRGO.

4.7.4 Experiments: Selective artificial photo-induced reduction of GO nano-sheets

In this part, and as a complementary study to the previous light photoinduced reduction investigations, selective frequency like-artificial radiations simulating the sun radiations were carried out. This was carried out in view of identifying the range of the spectral range controlling the oxydo-reduction phenomenon in GO nano-sheets based solutions.

4.7.4.1 Synthesis of graphene oxide nano-sheets

The graphite used in this work was purchased from Sigma-Aldrich. We synthesized graphene nanopowder using Hummers method which involved the exfoliation of graphite in the presence of strong acids and oxidants as described earlier. 1,5g of natural flake graphite powder was added to 35ml of cold (0 °C) concentrated H₂SO₄. Then, 4,5 g of KMnO₄ was added gradually with stirring and cooling in an ice bath. The mixture was then stirred at 40 °C for ~2h. Distilled water (70ml) was slowly added to the mixture and the temperature of the mixture was maintained below 100 °C for about 15min. After that, 210ml of 30% H₂O₂ solution was added to the mixture. Finally, the product was filtered with 400ml of 10% HCl aqueous solution to remove metal ions and then thoroughly washed five times with distilled water. Diluted solution of few layered graphene oxide (FLGO) was prepared by the dispersion (via ultrasound for ~ 1 hour) of 0,1g of the brown yellow powder in 200ml of distilled water. For samples preparation we filled 31 glass tubes with 10ml of FLGO solution for been exposed to sunlight, the 31st one was used as a reference sample. The various solutions were exposed to sunlight with selective filters for ~ 2 , ~ 4 , ~ 8 , ~ 16 and ~ 32 hours. For samples preparation we filled 17 glass tubes with 10ml of FLGO solution for been exposed to artificial light, the 17st one was used as a reference sample. The various solutions were exposed to artificial light with selective filters for ~ 2 , ~ 4 , ~ 8 and ~ 16 hours.

4.7.4.2 Artificial light irradiation

To realize this sunlight and artificial light exposure aqueous, graphene oxide suspensions, we prepared a system containing five standard halogen lamps (12V) emitting a white spectrum. Four of them were filtered to have

red, yellow, green and blue artificial emissions as shown in Figure 4.12. Each lamp has been used to irradiate a series of samples exposed for 2, 4, 8 and 16h simultaneously in the same time so to realize these experiences in similar conditions. The same method was followed for FLGO irradiation by sun light with a vertical inclination of samples position with 45° to insure a maximal effect. These experiences were carried out at room temperature and atmospheric pressure in order to avoid lights interference each lamp was encapsulated into an aluminum tube.



Figure. 4.12: filtered red, yellow, green and blue artificial emissions.

4.7.4.3 X-Rays Diffraction investigations

The crystallinity of the reduced graphene oxide by the sunlight or artificial light sources with different filters was investigated and compared with graphene oxide via the X-rays Diffraction (XRD) patterns of dried films deposited onto silicon substrates. **Figure 4.13** depicts a typical XRD profiles for various time of exposure obtained under sunlight or the artificial light sources.

The comparison of the typical peaks observed for the GO and RGO films showed the disappearance of GO peak and the appearance of peaks characteristics of reduced graphene oxide which found to be agglomerated as confirmed by the narrow FWHM peaks. The Dynamic of this reduction can be followed by the ratio of the two intensities I_1/I_2 that increases in value with the time of exposure due to the minimization of oxygen incorporation.

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Figure. 4.13: Typical XRD patterns of GO irradiated by sunlight and artificial light for different durations.

4.7.4.4 ATR-FTIR spectroscopy investigations

Figure 4.14 depicts ATR-FTIR patterns of GO irradiated by sunlight or artificial light sources with different filters for different durations. From the ATR-FTIR spectra, we see that the intensity of the carbonyl stretching band (1610cm⁻¹) decreases substantially after ~2 hours irradiation (**Figure 4.14**).

Similarly, the intensities of other bands due to other oxygen containing functional groups also decrease after the prolonged sunlight/artificial light sources with different filters irradiation. At 1620 cm⁻¹ (skeletal vibrations from un-oxidized graphitic domains), at 1220 cm⁻¹ (C-OH stretching vibrations), at 1060 cm⁻¹ (C-O stretching vibrations), and stretching vibrations from C=O at 1720 cm⁻¹ due to the remaining of carboxyl groups and the vibration modes of epoxide (C-O-C) at (1230-1320 cm⁻¹, asymmetric stretching at 850 cm⁻¹, bending motion).

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Figure. 4.14: Typical ATR-FTIR patterns of GO irradiated by sunlight and artificial light for different durations.

4.7.4.5 UV-Vis Absorbance spectroscopy investigations

The color change of the graphene oxide from brownish yellow to black is a clear evidence of the occurrence of reduction via sunlight or artificial light irradiation. The dynamic of photo-reduction by all radiations can be monitored easily with UV-UVIS absorbance spectroscopy. Indeed, the GO absorbance spectrum is known by the presence of three principal peaks, the main absorbance peak attributed to the $\pi \rightarrow \pi^*$ transitions of C-C occurs at around 225 nm, the broad absorption spectra extended up to 450 nm indicating a well-defined band-edge in the UV-VIS energy range and a shoulder around 320nm may be attributed to the $\pi \rightarrow \pi^*$ transitions of C-O. The Transformation of GO in our samples, reduced by sunlight as well as by artificial filtered light, is confirmed by the slow disappearance of C-C band centered at around 225 nm and its shifting to 260nm upon exposition time most likely due to the decrease in the concentration of carboxyl groups shown in Figure 4.15 indicating that the electronic conjugation within the reduced graphene sheets was revived upon reduction of graphene oxide.



Figure. 4.15: Typical UV-Vis absorbance spectra of GO irradiated by sunlight for different durations.

Figures 4.16-19. depict the UV-Vis absorbance spectra of the various photoreduced GO nano-solutions under both white light and filtered artificial light sources for various exposure time. It can be observed that the red filtered irradiated solution for various exposure time have roughly similar trend as the as prepared solution even after 16h of irradiation. In opposite, one could distinguish the significant effects of the yellow and blue filtered artificial radiations in addition to the well established white irradiation photoreduction phenomena. Indeed, as it is illustrated in Figure 4.16-19, the absorbance profiles of these radiations have similar trends. In all corresponding spectra, the specific absorbance in the UV-VIS range quasidisappear and are smoothened on a wide spectral range. This behavior seems to start at about the threshold exposure time of about 4. After 8h of irradiation, it seems that there is a stabilization of the photo-reduction process.

The process which is at the origin of this photo-induced chemical reduction sustain the explanation of *Rao et al* through a 3 phases mechanism.



Figure. 4.17: The various UV-VIS absorbance spectra of GO irradiated by different filtered artificial lights for 4h.



Figure. 4.18: The various UV-Vis absorbance spectra of GO irradiated by different filtered artificial lights for 8h.



Figure. 4.19: The various UV-Vis absorbance spectra of GO irradiated by different filtered artificial lights for 16h.

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[55]. Kumar K. S., Subrahmanyam C. N. R., Rao , J. Maters Science, 2012 Graphene produced by radiation-induced reduction of graphene oxide.



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4.9 CONCLUSION

The first objective of this thesis was to synthesize, characterize and investigate various properties of graphene or reduced graphene oxide. More specifically graphene oxide and reduced graphene oxide solutions prepared by Hummers method have been deposited on silicon substrates separately. Several techniques have been employed to characterize GO and RGO deposited on silicon substrates with the aim of investigating different properties of GO and rGO.

Hummers method is a cost efficient production method due to the price of raw materials but chemical processing completely introduces defects in the course of oxidation or reduction and functionalization in reduced graphene oxide sheets resulting to the decrease in conductivity [1] Thus the main challenge for accumulation of this process is to acquire routes for complete reformation of the sp² carbon network of reduced graphene oxide.

ATR-FTIR revealed the presence of OFG before reduction, after reduction the very same technique confirms fewer OFG in the reduced graphene oxide, this was further confirmed by the UV-Vis result when 225 nm absorption peak appeared after oxidation of graphite to graphene, the same peak shifted to 280 nm after reduction of graphene oxide to reduced graphene oxide. The 280 nm peak confirmed that most excess of oxygen functional groups have been removed. According to reference [2], the displaced peaks are due to the $\pi \rightarrow \pi^*$ transition for the C=C bonding.

The characterized films of GO and rGO exhibited the presence of OFG in AFM, results showed that GO has a lot of oxygen functional groups, this was

proved by the measured roughness of both GO and rGO. GO has a higher roughness than rGO which means there are more oxygen functional groups in GO which are stacked together than in rGO.

SEM showed some rippling and folding of stacked GO sheets before reduction, after reduction it showed wrinkled structure with less oxygen functional groups. TEM showed flake-like tightly packed GO sheets before reduction, after the reduction process the rGO sheets were stacked on top of one another to form a film. Raman spectrum showed D and G bands for both GO and rGO sheets but for rGO there is G* and 2D bands which are associated with the reduction process of GO to rGO.

All and all, the used techniques are in agreement, all displaced the expected information about graphene oxide and reduced graphene oxide.

The second objective of this project was to reduce GO using the sun and artificial light, more specifically GO solutions were exposed to sunlight for 2h , 4h, 8h, 16h and 32h. After 2h of irradiation the color changed from brownish yellow to black. The other durations also confirmed the color change. After irradiating GO for the above durations, three characterization techniques (XRD, ATR-FTIR and UV-VIS-NIR) were used to further confirm the reduction of GO. The obtained results were complementary to the previous results of *Rao et al* [3].

In the case of reducing GO using filtered artificial light, five lamps i.e green, blue, yellow, red and white were used to irradiate GO. GO solutions were exposed to each filtered artificial light as shown in figure 4.12. Each solution was exposed for 2h, 4h, 8h and 16h. The XRD, ATR-FTIR and UV-VIS

confirmed the reduction of GO. One can conclude that indeed using the sun and artificial light, we can produce graphene.



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4.10 References

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4.11 APPENDICES

4.11.1 APPENDIX A

Lattice structure	Hexagonal
Lattice constant (Å)	2.462
Atomic density (C atomic/ cm3)	1.14×10^{23}
Specific gravity (g / cm3)	2.26
Specific heat (cal/ g. K)	0.17
Thermal conductivity (W/ cm.K)	30 RSITY of the
Binding energy (eV/ C atom)WESTE	7.4 CAPE
Debye temperature (K)	2500 950
Bulk modulus (GPa)	1060 36.5
Bang gap (eV)	-0.04
Carrier density (10^{18} /cm ² at 4K	5
Electron mobility (cm ² / V sec)	20,000 100
Hole mobility (cm ² /V sec)	15,000 90

Resistivity (Ωcm)	50 X 10 ⁻⁶
Melting point (K)	4450

Appendix A: Properties of Graphite [13]

4.11.2 **APPENDIX B**

Lattice structure	Cubic
Lattice constant (Å)	3.567
Atomic density (C atoms/cm ³)	SITY of the 1.77×10^{23}
WESTER	N CAPE
Specific gravity (C atoms/cm3)	3.515
Specific heat (cal/g.K)	0.12
Thermal conductivity (W/cm. K)	~25
Binding energy (eV/ C atom)	7.2
Debye temperature (K)	1860
Bulk modulus (GPa)	42.2

Band gap (eV)	10
Carrier density (10 ¹⁸ /cm ³ at 4K)	0
Electron mobility (cm ² /V sec)	1800
Hole mobility (cm ² / Vsec)	1500
Melting point (K)	4500



Appendix B: Shows the summary of various properties of diamond [13]

4.11.3 APPENDIX C

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Hummers method uses chemicals and acids, below is the brief discussion of the chemicals and acids used for preparation.

POTASSIUM PERMANGANATE (KMnO₄)

Potassium permanganate is an inorganic chemical compound with the formula $KMnO_{4.}$ It is a salt of K^+ and $MnO_{4.}^-$ ions. Formerly known as permanganate potash, it is a strong oxidation agent. Potassium permanganate decomposes when exposed to light:

 $2 \text{ KMnO}_{4 (s)} \rightarrow K_2 \text{MnO}_{4 (s)} + \text{MnO}_{2(s)} + O_{2 (g)}$equation 9 Potassium permanganate is able to oxide primary alcohols to carboxylic acids Under acidic conditions the oxidation half-reactions are:

 $MnO_4^- + 4H^+ + 3e^- \rightarrow MnO_2^- + 2H_2O_4$ equation 10 $MnO_4^- + 8H^+ + 5e^- \rightarrow Mn2^+ + 4H_2O_4$ equation 11 Under alkaline conditions, the half-reaction is

 $MnO_4^- + 2H_2O_+ 3e^- \rightarrow MnO_2^- + 4OH^-$equation 12 Reaction rates for the oxidation of constituents found in natural waters are relatively fast and depend on temperature, pH and dosage

SULPHURIC ACID (H₂SO₄)

Sulfuric acid is a clear, colorless, viscous liquid that is very corrosive.

Sulfuric acid is often prepared as a byproduct from mining operations. Many metals ores are sulfides and smelting operations eliminate sulfur in the form of sulphuric dioxide gas. The sulphuric dioxide gas is cleaned and converted into sulphuric acid.

my substances.

HYDROGEN PEROXIDE (H₂0₂)

A mixture of H_2SO_4 and H_2O_2 is used to clean organic residues off substrates. Because the mixture is a strong oxide, it will remove most organic matter, and it will also hydroxylate most surfaces (add -OH groups), making them extremely hydrophilic (water compatible).

 $H_2SO_4 + H_2O_2 \rightarrow H_3O + HSO_4 + O....equation 15$

HYDROCHLORIC ACID (HCI)

HYDRAZINE HYDRATE (N₂H₄)

Hydrazine is an inorganic compound with the formula N_2H_4 . It is a colorless flammable liquid with an ammonia-like odor. Hydrazine is highly toxic and dangerously unstable unless handled in solution.

Hydrazine has basic (alkali) chemical properties comparable to ammonia:

 $N_2H_4 + H_2O \rightarrow N_2H_5 + + OH^-$equation 17 Hydrazine is a convenient reductant because the by-products are typically nitrogen gas and water thus; it is used as an antioxidant, an oxygen scavenger, and a corrosion inhibitor in water boilers and heating systems. It is also used to reduce salts and oxides to the pure metals in electrolysis nickel plating and plutonium extraction from nuclear reactor waste.

OXIDATION.

The purpose of adding H_2SO_4 in a solution is to increase the acidity of the solution and reacting acid with permanganate is to create MnO_3^+ that reacts with MnO_4^- to produce Mn_2O_7 as shown by the chemical reactions below.

 $KMnO_4 + 3H_2SO_4 \rightarrow K^+ + MnO^+_3 + H_3O^+ + 3HSO^-_4$equation 18

$MnO^{+}_{3} + MnO^{-}_{4} \rightarrow Mn_{2}O_{7}$equation 19

The formation of diamanganese heptoxide (Mn_2O_7) from $KMnO_4$ in the presence of strong acid is desirable since Mn_2O_7 is a strong oxidizing agent which is needed to oxidize graphite to graphite oxide.

By slowly adding potassium permanganate, the $Mn0^+_3$ ion reacts with the $Mn0^-_4$ resulting in dimanganese heptoxide Mn_20_7 which is a strong oxidizing agent, hence the reduction of graphite to graphite oxide.

 $Mn_2O_7 + H_2SO_4 \rightarrow MnSO_4 + 4H_2O + 5O_2$equation 20 Again, Sulphuric acid also assists in the conversion of hydrogen peroxide into hydronium ion and O radical which are aggressive oxidant

REDUCTION.

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The hydrazine hydrate dissociates in water to create a hydroxyl ion that reacts with oxygen in the graphitic structure after exfoliation process that resulted from oxidation to reduce graphene oxide to reduce graphene oxide . And the metal ions that are Mn^{2+} and K^+ will react with chlorine ion and the H^+ will react with the ⁻OH from hydrazine as follows.

$HCI \rightarrow H^+ + CI^-$ equation	21
$Mn^{2+} + 2Cl^{-} \rightarrow MnCl_{2}$ equation	22
$K^+ + Cl^- \rightarrow KCl$ equation	23



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