Graphene Oxide Material Interfaces in Electronics, Energy and Environmental Membranes

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**ABSTRACT**

The wonder material graphene promises to revolutionise countless applications as a result of its remarkable properties. However, an inability to process graphene in aqueous solution inhibits its potential for use in mass produced practical applications. This thesis investigates the use of graphene oxide (GO), a solution processable graphene based material produced from graphite in various applications. GO can be used to produce a graphene like material, reduced graphene oxide (rGO) which is also investigated. The scale up of GO is examined, showing no discernible difference to the final product with increasing batch sizes. By varying the concentration of oxidisers in the synthesis method, a series of GO materials with differing degrees of disorder and solution process ability are produced and characterised.

Using this series of GO materials, a model is proposed to explain the effect of the oxidation process on the GO flakes. Using Raman spectroscopy, a decrease in average sp$^2$ cluster size to approximately 1.2 nm is shown. This causes an increase in internal stress and structural disorder resulting in the broadening of the characteristic D and G peaks from 47 cm$^{-1}$ and 26 cm$^{-1}$ to 118 $\pm$ 6 cm$^{-1}$ and 72 $\pm$ 5 cm$^{-1}$, respectively. Thermogravimetric analysis (TGA) results confirm this increase in disorder, showing a decrease in the thermal decomposition temperature in air from 700$^\circ$C to 450$^\circ$C as oxygen in the atmosphere preferentially target sites of disorder. This analysis is used to determine the disorder present in a range of rGO samples, to determine the best material for use in various applications. The disorder present in GO also isolates sp$^2$ clusters, resulting in an increase in the band gap ranging from 0.02eV to 3.4 eV, while the reduction methods tested restore conjugation between isolated regions, causing the band gap to drop significantly.

GO is used as a hole transport layer in high efficiency organic photovoltaic (OPV) devices, producing power conversion efficiencies (PCE) of approximately 5% using the polymer blend Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2’,1’,3’-benzothiadiazole)]: Phenyl-C$_{70}$-butyric acid methyl ester (PCDTBT:PC$_{70}$BM) as the active layer. This represents an increase of 90% (+ 2.4% PCE) over devices without a hole transport layer, and results in similar efficiencies to devices using the standard material PEDOT:PSS. Additionally, due to the chemical stability of GO, the shelf lifetime of GO OPV devices is improved by 62% (+ 3200 hours) when compared with a reference PEDOT:PSS device.
Using a low temperature (< 250°C) simultaneous spray coating chemical reduction method; GO films are sprayed and chemically reduced on a surface using vitamin C, while the conductivity is monitored in real time. This allows for a conductivity increase of 5 orders of magnitude, resulting in thin films with $16.68\, \Omega/\square$ sheet resistance and 66.8% transmission (measured at 550nm). This conductivity ratio, i.e. the electrical conductivity divided by the optical conductivity ($\sigma_{\text{DC}}/\sigma_{\text{Op}}$), of 0.05 for the devices is comparable with other rGO based conducting networks reported, produced without the need for high temperatures, treated substrates or toxic reducing agents, making it practical for use on flexible plastic substrates. Importantly, Raman analysis of the thin films suggests that the conductivity of the rGO thin film is only partially limited by the disorder of the individual rGO flakes, with a significant proportion of the resistance originating from another source, i.e. flake to flake junctions.

GO materials are tested as environmental membranes for the adsorption of the textile dye Rhodamine B (RhB) absorbing as high as 106.5 mg per gram of GO adsorbent. Initial results suggest a link between the interlayer distance of GO based materials and their ability to quickly adsorb the dye. It is shown that by using a partially oxidised GO material, it is possible to adsorb the dye quickly (approx. 60 - 100 mg of dye adsorbed per gram of GO in 60 minutes), while minimising the GO left in solution (below 10 ppm stable in solution after 52 hours) reducing the likelihood of causing contamination. Furthermore, rGO based porous sponges are synthesised and, using SEM and X-ray CT, shown to be porous throughout, reducing the likelihood of contamination further because of the hydrophobicity associated with rGO materials.

Additionally, a hybrid rGO based material is synthesised, which contains iron nanoparticles of approximately 25 nm in diameter, encased in an iron oxide shell and impregnated in rGO sheets. This material (Fe-rGO) is shown to be magnetic, and is used in both OPV applications and for environmental adsorption. Finally, Fe-rGO porous sponges are produced, which could be revolutionary for use in environmental remediation. The magnetic properties allow for the adsorbing Fe-rGO to be removed from solution after adsorption, allowing 99% of the RhB dye to be recovered through elution in ethanol.
DECLARATION OF ORIGINALITY

I confirm that the submitted work is my own work and that I have clearly identified and fully acknowledged all material that is entitled to be attributed to others (whether published or unpublished). Any ideas, data, images or text resulting from the work of others are identified as such and attributed to the original author in the text, figure captions or the bibliography. I agree that the University may submit my work to means of checking this, such as the plagiarism detection service Turnitin® UK. I confirm that I understand that assessed work that has been shown to have been plagiarised will be penalised.

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Date  01/04/2016

Christopher T. G. Smith
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CONFERENCES PRESENTATIONS


# CONTENTS PAGE

ABSTRACT ................................................................................................................................. I  

DECLARATION OF ORIGINALITY .......................................................................................... III  

ACKNOWLEDGEMENTS ............................................................................................................ IV  

PUBLICATIONS ......................................................................................................................... VI  

CONTENTS PAGE ...................................................................................................................... VIII  

ABBREVIATIONS AND ACRONYMS ......................................................................................... X  

1 INTRODUCTION ...................................................................................................................... 1  
1.1 INTRODUCTION .................................................................................................................... 1  
1.2 THESIS OUTLINE .................................................................................................................. 5  

2 BACKGROUND, LITERATURE REVIEW AND INSTRUMENTATION ............................................. 6  
2.1 CARBON NANOMATERIALS .................................................................................................. 6  
   2.1.1 Overview ......................................................................................................................... 6  
   2.1.2 Graphene ....................................................................................................................... 11  
   2.1.3 Graphene Oxide ............................................................................................................ 15  
   2.1.4 Reduction of Graphene Oxide ....................................................................................... 19  
   2.1.5 Functionalization of Graphene Oxide Materials .......................................................... 23  
2.2 APPLICATIONS .................................................................................................................... 26  
   2.2.1 Overview ....................................................................................................................... 26  
   2.2.2 Transparent Conducting Electrodes ............................................................................. 27  
   2.2.3 Conduction Mechanisms ............................................................................................. 31  
   2.2.4 Organic Photovoltaics ................................................................................................. 36  
   2.2.5 Sorbent Materials ......................................................................................................... 47  
2.3 INSTRUMENTATION ............................................................................................................. 51  
   2.3.1 Raman Spectroscopy .................................................................................................... 51  
   2.3.2 Thermogravimetric Analysis ....................................................................................... 54  
   2.3.3 X-Ray Diffraction ....................................................................................................... 56  
   2.3.4 Ultra Violet – Visible Spectroscopy ............................................................................ 59  
   2.3.5 Fourier Transform Infrared Spectroscopy .................................................................... 61  
   2.3.6 Imaging Techniques ..................................................................................................... 62  
   2.3.7 X-Ray Computed Tomography .................................................................................. 63  
2.4 SUMMARY ............................................................................................................................ 65  

3 THE SYNTHESIS AND CHARACTERISATION OF GRAPHENE OXIDE MATERIALS ................. 66  
3.1 INTRODUCTION .................................................................................................................... 66  
3.2 SYNTHESIS OF GRAPHENE OXIDE BASED MATERIALS .................................................. 66  
3.3 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA RAMAN ................................ 68  
3.4 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA TGA .................................... 76  
3.5 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA XRD ..................................... 81  
3.6 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA UV-Vis ................................. 88  
3.7 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA FTIR ....................................... 95  
3.8 SUMMARY ............................................................................................................................ 97  

4 THE SYNTHESIS AND CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS .... 99  
4.1 INTRODUCTION .................................................................................................................... 99  
4.2 SYNTHESIS OF REDUCED GRAPHENE OXIDE BASED MATERIALS ................................... 99  
4.3 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA RAMAN ................ 101  
4.4 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA TGA ..................... 108  
4.5 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA XRD ...................... 114  
4.6 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA UV-Vis .................. 116  
4.7 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA FTIR ................... 121
5 GRAPHENE OXIDE MATERIAL INTERFACES IN ORGANIC PHOTOVOLTAIC APPLICATIONS ........................................ 125
5.1 INTRODUCTION .................................................................................................................................................. 125
5.2 MATERIALS AND METHODS FOR PRODUCING GRAPHENE OXIDE INTERFACIAL LAYERS IN ORGANIC PHOTOVOLTAIC ........................................................................................................... 125
5.3 IMAGING CHARACTERISATION OF GRAPHENE OXIDE THIN FILMS ................................................................ 127
5.4 GRAPHENE OXIDE INTERFACIAL LAYERS IN ORGANIC PHOTOVOLTAICS ...................................................... 129
5.5 GRAPHENE OXIDE ORGANIC PHOTOVOLTAIC LIFETIME TESTING ............................................................. 136
5.6 GRAPHENE OXIDE ORGANIC PHOTOVOLTAIC CONDUCTION MECHANISMS .................................................. 140
5.7 IRON - REDUCED GRAPHENE OXIDE INTERFACIAL LAYER IN ORGANIC PHOTOVOLTAIC ................................ 147
5.8 SUMMARY ......................................................................................................................................................... 149
6 GRAPHENE OXIDE MATERIAL INTERFACES FOR THIN FILM APPLICATIONS .................................................. 150
6.1 INTRODUCTION .................................................................................................................................................. 150
6.2 PRODUCTION AND CHARACTERISATION OF REDUCED GRAPHENE OXIDE THIN FILMS .................................... 150
6.3 CONDUCTIVITY TESTING OF REDUCED GRAPHENE OXIDE THIN FILMS ....................................................... 152
6.4 OPTICAL PROPERTIES OF VITAMIN C REDUCED GRAPHENE OXIDE THIN FILMS ........................................... 158
6.5 VITAMIN C REDUCED GRAPHENE OXIDE TRANSPARENT CONDUCTING ELECTRODES .................................. 160
6.6 SUMMARY ......................................................................................................................................................... 162
7 GRAPHENE OXIDE MATERIALS FOR ENVIRONMENTAL MEMBRANES ............................................................ 164
7.1 INTRODUCTION .................................................................................................................................................. 164
7.2 ADSORPTION OF RHODAMINE B USING GRAPHENE OXIDE .............................................................................. 164
7.3 SYNTHESIS OF REDUCED GRAPHENE OXIDE SPONGES .................................................................................. 169
7.4 RAMAN ANALYSIS OF REDUCED GRAPHENE OXIDE SPONGES ..................................................................... 171
7.5 IMAGING OF REDUCED GRAPHENE OXIDE SPONGES ................................................................................... 173
7.6 ADSORPTION OF RHODAMINE B USING REDUCED GRAPHENE OXIDE SPONGES ......................................... 182
7.7 MAGNETIC REDUCED GRAPHENE OXIDE ADSORBERS ................................................................................... 185
7.8 SUMMARY ......................................................................................................................................................... 190
8 CONCLUSIONS AND FUTURE WORK .................................................................................................................... 193
8.1 CONCLUSIONS .................................................................................................................................................. 193
8.2 FUTURE WORK .................................................................................................................................................. 195
9 REFERENCES ......................................................................................................................................................... 199
10 APPENDICES ....................................................................................................................................................... 210
10.1 IR COMPARISON TABLE .................................................................................................................................. 210
10.2 XRD PEAK ASSIGNMENTS FOR THE GO\textsubscript{MRH05} SERIES ...................................................................... 211
10.3 HANSEN SOLUBILITY PARAMETERS .............................................................................................................. 211
10.4 CONTACT ANGLE MEASUREMENTS .................................................................................................................. 212
10.5 CONDUCTION MECHANISM DERIVATIONS .................................................................................................... 213
10.6 ADDITIONAL REDUCED GRAPHENE OXIDE RAMAN SPECTRA ...................................................................... 216
10.7 REDUCED GRAPHENE OXIDE SPONGE CONTRAST CT SCAN ........................................................................ 218
10.8 ADDITIONAL IMAGES OF IRON NANOPIRCLE – REDUCED GRAPHENE OXIDE .................................................. 220
# Abbreviations and Acronyms

## Materials

- **BCP** – Bathocuproine
- **CNT** – Carbon nanotube
- **HOPG** – Highly ordered pyrolytic graphite
- **IPA** – Iso-propanol
- **ITO** – Indium tin oxide
- **GO** – Graphene oxide
- **P3HT** – Poly(3-hexylthiophene-2,5-diyl)
- **PC60BM** – Phenyl-C60-butyric acid methyl ester
- **PC70BM** – Phenyl-C70-butyric acid methyl ester
- **PCDTBT** – Poly[N-9′-heptadecanyl-2,7-carbazole-alt-5,5-(4′,7′-di-2-thienyl-2′,1′,3′-benzothiadiazole)]
- **PEDOT:PSS** – Poly(3,4-ethylenedioxythiophene) polystyrene sulfonate
- **PET** – Polyethylene terephthalate
- **PPV** – Poly(p-phenylene vinylene)
- **RhB** – Rhodamine B
- **rGO** – Reduced graphene oxide

## Instrumental Techniques

- **AFM** – Atomic Force Microscopy
- **CVD** – Chemical Vapour Deposition
- **EQE** – External Quantum Efficiency
- **FTIR** – Fourier Transform Infrared Spectroscopy
- **PL** – Photoluminescence Spectroscopy
- **SEM** – Scanning Electron Microscopy
- **TEM** – Transmission Electron Microscopy
- **TGA** – Thermogravimetric Analysis
- **TLM** – Transmission Line Measurement
- **UV-Vis** – Ultra Violet – Visible Spectroscopy
- **X-ray CT** – X-ray Computed Tomography
- **XRD** – X-ray Diffraction

## Technical Abbreviations

- **A** – Modified Richardson Constant
- **C** – Concentration or Constant
- **d** – Distance (or d spacing)
- **e** – Elementary Charge
- **E** – Electric Field
- **E_b** – Interlayer Bonding Energy
- **E_F** – Fermi Level
- **ε_0** – Vacuum Permittivity
- **ε_r** – Relative Permittivity
- **ETL** – Electron Transport Layer
- **FF** – Fill Factor
- **GW** – Giga Watt
- **h** – Plancks’ Constant
- **H_c** – Magnetic Coercivity
- **HOMO** – Highest Occupied Molecular Orbital
- **HTL** – Hole Transport Layer
- **I** – Current or Intensity
- **J** – Current Density
- **J_sc** – Short Circuit Current Density
- **k** – Boltzmann Constant or Rate Constant
- **κ** – Tunnelling Probability
- **LUMO** – Lowest Unoccupied Molecular Orbital
- **m^*** – Effective Mass of a Charge Carrier
- **M_s** – Saturation Magnetism
- **μ** – Mobility
- **n_0** – Number of Free Carriers
- **ν** – Frequency
- **OPV** – Organic Photovoltaic
- **PCE** – Power Conversion Efficiency
- **P_in** – Input Power
- **P_max** – Maximum Power
- **PV** – Photovoltaic
- **ρ** – Resistivity
- **q_e** – Quantity adsorbed at equilibrium
- **q_t** – Quantity adsorbed at time t
- **R** – Resistance
- **R_p** – Parallel Resistance
- **R_s** – Sheet Resistance
- **R_{ss}** – Series Resistance
- **σ_{dc}** – 3 Dimensional Conductivity
- **σ_{op}** – Optical Conductivity
- **t** – Time
- **T** – Temperature
- **T_{op}** – Optical Transmission
- **V** – Voltage
- **V_{oc}** – Open Circuit Voltage
- **ϕ_{WF}** – Work Function
- **ϕ_W** – Barrier Height
- **Z_0** – Impedance of Free Space
Conduction Mechanisms

FN – Fowler Nordheim Tunnelling
PF – Poole Frenkel Effect
Sch – Schottky Emission
SCLC – Space Charge Limiting Current

Experimental Terminology

A_D – Integrated area of the D peak
A_G – Integrated area of the G peak
FWHM_D – Full Width Half Maxima of the D peak
FWHM_G – Full Width Half Maxima of the G peak
I_D – Intensity of the D peak (Raman)
I_G – Intensity of the G peak (Raman)
\lambda – Wavelength
C(\lambda) – Wavelength Dependent Constant
L_a – Average size of sp^2 clusters / Crystallites
TK – Tuinstra and Koenig Equation

Thesis Specific Acronyms

Fe-rGO – Reduced graphene oxide decorated with iron nanoparticles
GO_HMX – Graphene oxide synthesised by the Hummers’ method, where x increases with batch size
GO_MRHXX – Graphene oxide synthesised by a mixed ratio Hummers’ method, where xx is used to describe the ratio of graphite to oxidiser (i.e. GO_{MHR12} 1:2 graphite to oxidiser ratio)
rGO_{sol} – Graphene oxide reduced via a solar photothermal reduction method
rGO_{TA} – Graphene oxide reduced via a thermal reduction method
rGO_{VC} – Graphene oxide reduced via a vitamin C chemical reduction method
1 INTRODUCTION

1.1 INTRODUCTION

As citizens of planet earth, it is humanity’s civic responsibility to preserve the planet for future generations. The Paris agreement (COP21), globally adopted by 195 countries in December 2015, aims to reduce the emission of greenhouse gases, primarily carbon dioxide (CO$_2$) and methane (CH$_4$), by 60% by 2050 in order to curb the increase in global average temperature to below 2°C above pre-industrial levels.$^1$ Speaking of the Paris agreement, Prof. Jeffrey Sachs, director of the Earth institute at Columbia university said, “The diplomats have done their job: the Paris Agreement points the world in the right direction, and with sophistication and clarity. It does not, however, ensure implementation, which necessarily remains the domain of politicians, businessmen, scientists, engineers, and civil society.”

The implementation of new materials in applications adapted to combat climate change is essential for future development. Enter graphene, the “wonder material” isolated in 2004, which led its discoverers to win the Nobel Prize in Physics in 2010.$^2$ With remarkable properties, including incredible strength, optical transparency and ballistic electrical conduction, graphene represents a platform material for the enhancement of various technologies. However, an inability to process graphene in aqueous solution inhibits its potential for use in mass produced practical applications. In contrast, graphene oxide (GO), a chemically modified material made from natural graphite, which can be reduced in various ways to give graphene like platelets, commonly known as reduced graphene oxide (rGO), is solution processable in environmentally friendly solvents (i.e. water). However, the chemical modification required to form both GO and rGO platelets also causes a reduction in some of the favourable properties of graphene. Understanding the effect of these chemical modifications, in both the initial oxidation and later reduction stages, is essential to allow for implementation of these materials in environmentally friendly applications.
One potential method for implementation examined is the enhancement of renewable energy technologies with an aim to reduce the world’s current dependence on fossil fuels. Numerous options are under development, including hydro-electric dams, alternative fuels from biomass, wind power and tidal generators. Possibly the fastest growing renewable energy alternative comes in the form of solar power. Utilising the abundant energy provided by the sun, solar harvesting technology can be used to both heat water, through solar heating installations, and directly provide electricity, through the use of photovoltaic (PV) devices.

As of 2014, photovoltaic installations were estimated to contribute approximately 177 Giga Watts (GW) of electricity, contributing more than 1% of the global electricity supply. That is over ten times the amount contributed in 2008 and a hundred times the amount contributed in 2003 (14.6 GW and 1.6 GW respectively). This exponential growth in the PV industry is fuelled by decreases in production costs and government initiatives, leading a to significant decrease in the cost of electricity generated through PV.

The first silicon PV solar cell demonstrated in 1954 comprised of thick layers of doped crystalline silicon, which are capable of generating high power conversion efficiencies (PCE)
but with high fabrication costs. This type of device is often termed the first generation (1G) of photovoltaic devices. The high processing costs associated with the purification of silicon, and the large quantities of materials needed, led to the development of the second generation (2G) of PV that attempted to mitigate these aspects. 2G solar cells utilised ultra-thin films of absorbing materials to lower the cost associated with the 1G solar cell. However, while the cost was reduced, so too were the PCEs due to the higher disorder in the inorganic materials affecting its physical properties. This led to the development of third generation (3G) solar cells, which combine multi-junction architectures with alternative materials, in order to increase efficiencies while maintaining low production costs.

Organic thin film photovoltaics (OPV), which fall into the 3G category of solar cells, are comprised of various conjugated polymers or small molecules, and fullerene materials. These cheap materials, which can be processed in solution, show promise for cheap mass production. However, current OPV devices demonstrate low PCEs and shorter lifetimes when compared with silicon counterparts. Utilising GO based materials to improve device efficiency and lifetime could result in increases in the cost effectiveness of PV technology, increasing the chances of adoption and implementation.

The electrical properties of graphene make it an ideal candidate for use in transparent thin film electronics. Thin film electronics utilise thin electrically conducting layers for applications such as flat panel displays, touch screens and solar cells. Improving on existing material systems have significant environmental ramifications, as increases in device efficiency will result in a lowering of the amount of power used by the device while improvements to device lifetime lower the environmental impact of replacement.

The current transparent conducting electrode of choice, indium tin oxide (ITO) is brittle and cracks under flexing. The price of indium in 2014 reached as high as $700 per kg, with prices in constant flux due to the ever increasing demand. The advent of smartphones, tablets and other touch screen mobile devices, have dramatically increased the demand for indium, putting strain on supply capacity. Therefore, a cheap alternative, making use of a stable abundant natural resource such as graphite is favourable for future development.

Replacing ITO with a conductive and transparent alternative is essential for realising cheap or flexible optoelectronic applications. Flexible electronics open up a large variety of niche
applications, such as wearable electronics and folding solar panels for satellites. Plastic substrates hold the key to flexible electronics, which limits the processing temperature available for use to low temperatures (< 250°C). Various materials are in development as alternatives to ITO; including metal oxides such as aluminium zinc oxide, metal networks such as silver nanowires or gold metallic grids, and carbon based alternatives such as conducting polymers, carbon nanotubes (CNTs) or chemical vapour deposition (CVD) grown graphene.

Another way GO materials can be used to aid the environment is through environmental clean-up and water filtration. This can be achieved through the use of three dimensional (3D) porous structures that can be made using GO. These porous sponge structures could prove invaluable in the clean-up of oil spills, as well as removal of various pollutants from water systems. Oil remediation operations typically involve skimming oil from the surface of spills, and then the application of toxic detergents to disperse the remnant. This combination is only partially effective, devastating local ecosystems and the environment as a whole. Methods of improved oil remediation are imperative in negating the damage caused by oil slick disasters.

Commercially available water filters are commonly made from a material called activated carbon, in which carbon based materials such as wood, coal or organic are pyrolyzed at high temperatures (600 - 900°C) to open up porous throughout the structure, making it an energy intensive process which could be improved upon. Additionally, the high temperature requirements restrict the ability for people to make activated carbon where it is needed. Therefore the development of alternative adsorbent materials is essential for supplying clean water in remote areas. Overall, the wide range of potential environmentally friendly applications capable of using materials such as GO merit further investigation.
1.2 Thesis Outline

This thesis will explore the use of solution processable, chemically modified GO materials, primarily GO and rGO, in various environmental applications. Following this introductory chapter, Chapter 2 will provide a detailed review of carbon nanomaterials, especially graphene based materials, followed by a brief look at possible applications for the graphene materials. This will primarily focus on three applications; transparent conductors, interfacial layers in OPV and adsorbent materials for environmental remediation, which will be explored in further depth in subsequent chapters. Finally, Chapter 2 will summarise the fundamentals of the characterisation techniques used throughout the thesis. Chapter 3 looks at a series of GO based materials, using a variety of characterisation methods, to give an insight into the oxidation process. Similarly, Chapter 4 investigates a variety of environmentally friendly reduction methods capable of being used to produce large quantities of rGO materials at a low cost.

Chapters 5, 6 and 7 look at using the materials produced in Chapters 3 and 4 in a selection of applications. Chapter 5 focuses on the use of GO materials in OPV devices, while Chapter 6 investigates the use of spray coated rGO as transparent conducting electrodes. Chapter 7 details the production of porous 3D structures of rGO, and compares them with other GO based materials for use as adsorbent materials in the removal of pollutant dyes from water sources. To conclude, Chapter 8 summarises the conclusions of the thesis, and proposes topics for future consideration.
2 BACKGROUND, LITERATURE REVIEW AND INSTRUMENTATION

2.1 CARBON NANOMATERIALS

2.1.1 OVERVIEW

The discovery of the C₆₀ Buckminsterfullerene in 1985 sparked a revolution in the field of carbon materials. In the 30 years that followed, the allotropes of carbon expanded from just graphite and diamond, to a wide range of nanomaterials in various shapes and sizes. A nano-material is defined as a material that contains particles with at least one dimension in the nanoscale range, considered to be between 1 - 100 nm (10⁻⁹ m). This is significantly smaller than the microscale and leads to interesting quantum effects. These quantum effects arise due to a phenomenon known as ‘size quantisation’ which occurs in the nanometer range. This phenomenon, often explained using the particle in a box model, is caused by the confinement of movement of electrons and leads to the formation of discrete energy levels or orbitals. These energy levels were the basis of the Bohr atom model in 1913 as represented in Figure 2.1.1.

![Figure 2.1.1: The Bohr Model of the Atom showing discrete energy level orbitals (n = 1, 2, 3 etc.) n = ∞ represents the vacuum energy level i.e. the energy required to remove an electron from the outer shell of the atom.]

However, the Bohr atom model failed to take into account the Heisenberg uncertainty principle, which states that it is not possible to know the exact position and momentum of an electron simultaneously. To take into account the uncertainty principle, orbitals were
redefined as regions in 3D space where the probability of finding the electron is above a certain value (95%). These atomic orbitals are characterised by a set of quantum numbers n, l, and m which define the energy of the electron, and the shape and orientation of the orbital. The shape of orbitals, as defined by the quantum number l, is important to understanding many of the properties of carbon nanomaterials. The shapes of the s and the 3 degenerative p orbitals, which are important when dealing with carbon materials, are shown in Figure 2.1.2. It is the overlapping of these orbitals which leads to the creation of covalent chemical bonds.

\[ \text{FIGURE 2.1.2 THE SHAPES OF THE } s \text{ AND } p_x, p_y, \text{AND } p_z \text{, ATOMIC ORBITALS AND THE ELECTRON CONFIGURATION OF A CARBON ATOM IN ITS GROUND STATE. A RED ARROW REPRESENTS A SINGLE ELECTRON.} \]

The electronic configuration of the six electrons in a standard carbon atom, is 1s\(^2\), 2s\(^2\) and 2p\(^2\). Standard covalent bonds are formed when two atomic orbitals containing one electron each overlap, allowing a sharing of the electron between the two nuclei. In its ground state, carbon has two atomic orbitals which contain one electron each which could be used for bonding. However, because the energy difference between the 2s orbital and the 2p orbitals is so small, it is energetically favourable for one of the electrons in the 2s orbital to jump into the unoccupied 2p orbital, allowing for the creation of 4 equal bonds through a process called ‘orbital hybridisation’. This is the process where the 2s and the 2p orbitals hybridise to form sp, sp\(^2\) and sp\(^3\) orbitals, depending on how many p orbitals combine with the s orbital. This allows the carbon atoms to bond to multiple other elements to form a variety of compounds, as the bond hybridization allows for carbon atoms to bond to 2, 3 or 4 neighbouring atoms equally. The bond hybridization, for sp\(^2\) and sp\(^3\) carbon atoms, is demonstrated in Figure 2.1.3.
The sp<sup>2</sup> and sp<sup>3</sup> orbitals are very significant when looking at carbon nanomaterials, as they can be used to explain the two original carbon allotropes, diamond and graphite. Diamond is made completely of sp<sup>3</sup> carbon atoms (Figure 2.1.3), with each carbon atom bonded to 4 neighbouring carbon atoms in a tetrahedral formation. Alternatively, graphite is made up of multiple flat sheets of sp<sup>2</sup> carbon atoms stacked on top of each other. In graphite sheets, each carbon atom is bonded with three neighbouring carbon atoms in a trigonal planar formation, forming a two dimensional hexagonal lattice. The difference in bonding type between diamond and graphite has major implications on the properties of both, particularly the electrical properties. Diamond as a material is electrically insulating, while graphite is electrically conductive, albeit only in two dimensions. This electrical conductivity in graphite is a result of the free electron in the p<sub>z</sub> orbital which sits above and below the plane of sp<sup>2</sup> bonding (Figure 2.1.3). The combination and delocalisation of these p<sub>z</sub> orbitals on each carbon atom allows for electrical conduction along the graphite sheet.

In order to have covalent chemical bonding, electrons must be shared between atoms. This is achieved by combining orbitals, either via end to end overlap, also known as sigma bonding, or side to side overlap, known as π bonding. In diamond, two sp<sup>3</sup> orbitals overlap to form a sigma bonding (σ) and a sigma anti-bonding (σ*) orbital between each carbon atom. The electrons occupy the bonding orbital which is a lower energy conformation, thus creating a C - C σ bond. With sp<sup>2</sup> carbon materials such as graphite, sp<sup>2</sup> orbitals overlap to form a C – C σ bond much like in diamond; however the p<sub>z</sub> orbitals can also form delocalised...
π bonds with neighbouring carbon atoms. In the case of benzene which has six sp² carbon atoms bonded together in a ring, this creates three pi (π) bonding orbitals and three π* anti-bonding (π*) orbitals. When this is extended to graphite, which contains a much larger number of carbon atoms, the π bonding orbitals are easier to consider as a band of orbitals as shown in Figure 2.1.4. The energy difference between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) is negligible, and therefore electrons can easily be raised from the HOMO level to the LUMO level to facilitate charge transport. Therefore, graphite can be considered a semi-metal which leads to the conductivity in graphite as previously discussed.\(^{23}\)

![π Molecular Orbital Diagrams](image)

**Figure 2.1.4** π Molecular Orbital Diagrams for Ethene, Benzene and Graphite, Showing the Increasing Number of π Orbitals Formed, Resulting in the Formation of a Band of Orbitals When \(n\) Approaches Infinity. The red part of the band represents orbitals filled with electrons. The sp² C - C σ bonds are neglected for simplicity.

The energy of the HOMO and LUMO levels and the difference between them, also known as the band gap, are used to determine the electrical conduction properties of a material. If the gap between the HOMO and the LUMO level is very large, a lot of energy is required to promote an electron into the LUMO level, therefore restricting the movement of the electron, which in turn makes the material an insulator. If the band gap is small, electrons can easily be excited from the HOMO to the LUMO level, via addition of light or heat for example. These materials are classified as semi conducting materials. If the band gap is negligible, like in the case of graphite, then the material is considered a metal or semi-metal. The Fermi level (\(E_F\)) is defined as the electrochemical potential for electrons in the material. In the context of band theory, this relates to a hypothetical energy level between the HOMO and LUMO levels, where the probability of the energy level being filled is 50%.\(^{24}\) The work function (\(\phi_{WF}\)) of a material can then be defined as the energy difference between the Fermi level and the vacuum energy level (\(n = \infty\)) of the material. The band diagrams for various types of material are shown in Figure 2.1.5.
The semi-metal like conductivity observed in graphite also transfers to other graphite based nanomaterials such as fullerenes, CNTs, and graphene, which are made up of sp² bonded carbon atoms much like graphite. As previously stated, graphite is made up of flat sheets of sp² carbon atoms stacked on top of each other. These individual layers are given the name graphene, and are only one carbon atom thick. CNTs can be subsequently considered as one graphene sheet rolled into a tube shape, whereas a fullerene, of which the C₆₀ Buckminsterfullerene was the first to be discovered, can be considered as a graphene sheet rolled into the shape of a ball. Therefore, the properties that relate to graphene have wide reaching implications in all carbon nanomaterials, whether looking at graphite, fullerenes, or CNTs.
2.1.2 Graphene

An individual sheet of graphite, the material also known as graphene, was first isolated in 2004 at the University of Manchester by physicists Geim and Novoselov. This and following experiments with graphene led to the pair receiving the Nobel Prize in Physics in 2010. The electrical properties of the individual graphene sheet isolated were remarkable, with electron and hole concentrations of approximately $10^{13}$ cm$^{-2}$. When an electron is promoted into an excited state, it leaves a vacancy in the orbital it previously occupied. This is referred to as an electron hole.

Due to graphene’s atomic thickness, it absorbs only 2.3% light per layer making it virtually transparent. This coupled with its electrical properties make it a very interesting material for next generation electronics. Through nano-indentation on a defect-less flake of graphene, it has also demonstrated incredible intrinsic strength and elasticity. These properties make graphene an ideal candidate for use in flexible electronics.

However, the major problem limiting the use of graphene in applications is the production method. The original isolation of graphene films in 2004 was accomplished through the repeated delamination of highly ordered pyrolytic graphite (HOPG) using scotch tape. This
mechanical exfoliation method, while easy to implement, is not time effective or scalable to the large quantities required for mass production of applications. Other mechanical methods have been proposed in the literature.\textsuperscript{28} However, control of the flake thickness is not easy, and such techniques often require high temperatures to remove chemical adhesives used in the process making them unsuitable for plastic substrates which would be required for flexible applications.

Another common method of graphene film synthesis is epitaxial growth via chemical vapour deposition (CVD). Growing graphene via CVD involves depositing carbon based gases such as methane onto a catalytic transition metal surface, e.g. copper, cobalt or nickel. A combination of hydrogen gas and carbon feeder gas flow into a vacuum chamber in the presence of the catalyst and react to deposit carbon atoms on the catalyst surface. This method has been shown to be very effective at producing high quality graphene.\textsuperscript{29} Most methods require very high temperatures (\(>700^\circ\text{C}\)), although lower temperature alternatives are being developed. Using a photo-thermal CVD process it is possible to produce graphene films with a reported sheet resistance of 790 \(\Omega/\square\). with an optical transmission of over 90%.\textsuperscript{30} However, in all epitaxial growth methods, the grown films require delamination from the metal catalyst and a transferring step before it can be used on the target substrate.

One of the major routes for graphene material synthesis is the chemical exfoliation of graphite. This requires overcoming graphite’s interlayer bonding energy, allowing for separation of individual sheets. Through experimental investigation, the interlayer bonding energy \((E_b)\) for graphite has been determined as 42.6 meV per atom at an interlayer distance of 3.35 Å.\textsuperscript{31} This bonding energy is the result of a series of electrostatic and dipole interactions designated Van Der Waals forces. The delocalised \(\pi\) bonds caused by the \(p_z\) orbitals can create temporary dipoles above and below individual graphene sheets, which will induce dipoles on neighbouring sheets, and so on throughout the rest of the graphite layers (Figure 2.1.7). Chemical exfoliation focuses on disrupting the Van Der Waals interactions, allowing for separation of individual layers.
Chemical exfoliation of graphite can be sub-divided into 3 main categories. The first, labelled as direct solvent exfoliation involves finding a suitable solvent that can intercalate in between the layers, disrupting the induction of dipoles and therefore lowering the interlayer binding energy. Various solvents have been suggested in the literature to achieve this, including 1-propanol, N-methyl-2-pyrrolidinone (NMP) and N,N-dimethylformamide (DMF). It is shown in literature that solvents can be discerned using Hansen solubility parameters. The Hansen solubility parameters are used to quantify the intermolecular interactions as shown in Equation 1. The parameters sum the total of the energy for dispersive forces (such as Van der Waals interactions), \( E_{C,D} \) for polar forces \( E_{C,P} \), and for hydrogen bonding \( E_{C,H} \).

\[
\delta_i^2 = \delta_T^2 + \delta_D^2 + \delta_p^2 + \delta_H^2 \\
where \delta_i = \frac{E_{C,i}}{V_m} \quad (Equation \ 1)
\]

where \( E_c \) is the energy of cohesion, \( V_m \) is the molar volume and \( I \) represents T, D, P and H which stand for the total, dispersive, polar and hydrogen bonding contributions respectively. The Hansen parameters are then taken as the square root of these components. For a solvent to be good at dispersing a material, all 3 components of the Hansen parameters must be similar to the solute. In the case of graphite, the binding energy

\[ E_b \]
and the cohesive energy can be considered the same. The Hansen solubility parameters for graphene are $\delta_D \sim 18 \text{ MPa}^\frac{1}{2}$, $\delta_p \sim 9.3 \text{ MPa}^\frac{1}{2}$ and $\delta_H \sim 7.7 \text{ MPa}^\frac{1}{2}$ resulting in a final sum (also called the Hildebrand solubility parameter) of $\delta_T \sim 23 \text{ MPa}^\frac{1}{2}$ as detailed in literature.\(^{36}\)

One of the major disadvantages of direct solvent exfoliation is the sonication time required in order to achieve a monodisperse solution at high concentrations. Frequently samples contain only small amounts of monolayer graphene, with the majority of the sample containing few layer graphite particles. These few layer graphite materials are nearly impossible to separate from the monolayer graphene flakes owing to their similar size, weight and structure. Another disadvantage with this method is the solvents used are often very harmful and/or toxic to the environment. For example, one of the best solvents for creating stable graphene solutions from graphite is chlorosulphonic acid, capable of creating 2 mg/mL solutions without the need for sonication.\(^{37}\) However chlorosulphonic acid is highly toxic, and a powerful lachrymatory agent, commonly referred to as a tear gas, and therefore is not suitable for industrial applications.

Another common method for exfoliating graphene from graphite is to use surface active agents or surfactants. Most surfactants are amphiphilic compounds with both a hydrophilic (water attracting) and a hydrophobic (water repelling) end which bridges the gap between the hydrophobic graphene and the water solvent. This method has the advantage of using much more environmentally friendly solvents, such as water in order to achieve a stable dispersion.\(^{38}\) One of the most notable methods developed recently was the use of a combination of surfactants and shear mixing to demonstrate graphite exfoliation.\(^{39}\) This method exhibited scale up potential as large quantities of graphene like material could be processed simultaneously. It should be noted that the exfoliation by surfactant is not 100% successful, often producing few layer graphite materials dispersed in the solution. For example, in the case of surfactant combined with shear mixing, the measured thickness of the final flakes was less than 10 layers thick, however only approximately 10% of the flakes were monolayer.\(^{39}\) The use of surfactant exfoliation is promising because of the high quality graphene materials which can be created. However, the presence of additional surfactant chemicals surrounding the graphene flakes is likely to disrupt the desired electronic properties, unless it is possible to remove the surfactant post deposition. Unfortunately, if
the surfactant is removed after exfoliation but before deposition, the van der Waals interactions will cause multilayer flakes to reform.

The final type of chemical exfoliation is the functionalization of the graphite material itself, to aid in exfoliation and promote dispersion into environmentally friendly solvents. This overcomes the issue of flake reformation seen in surfactant exfoliation, often at the expense of the quality of the material. The most commonly used method is to oxidise graphite into graphite oxide, which can easily be exfoliated into individual GO sheets and then reduced back to a graphene like material, termed reduced graphene oxide (rGO), after deposition. A schematic for this is method is shown in Figure 2.1.8.

![Schematic of chemical exfoliation of graphite through the production of graphene oxide](image)

**FIGURE 2.1.8 SCHEMATIC REPRESENTATION OF THE CHEMICAL EXFOLIATION OF GRAPHITE THROUGH THE PRODUCTION OF GRAPHENE OXIDE. THE BLACK, RED AND WHITE ATOMS REPRESENT CARBON, OXYGEN AND HYDROGEN (IN WATER) RESPECTIVELY.**

2.1.3 **Graphene Oxide**

The synthesis of graphite oxide was first proposed by Brodie in 1859. The method used a combination of fuming nitric acid and chlorate of potash, more commonly known as potassium chlorate, to exfoliate and oxidise layers from graphite. A similar method of graphite oxide synthesis was proposed by Staudenmaier in 1898, in which sulphuric acid is also added to the nitric acid, graphite, and potassium chlorate used in the Brodie method. This method was tweaked by Hoffman in the 1930s, using a lower concentration of nitric acid. His group also proceeded to describe the structure of graphite oxide in some detail. Possibly the most famous method for graphite oxide synthesis is the Hummers’ method, which was developed in 1958. This method uses a similar concept to the original Brodie
method, but replaces the fuming nitric acid and explosive potassium chlorate with sulphuric acid, sodium nitrate and potassium permanganate as the reagents used to oxidise the layers of graphite. Hummers’ method is often modified to increase its effectiveness, for example by increasing the amount of potassium permanganate, or by replacing sodium nitrate with phosphoric acid.\textsuperscript{45}

The principle behind the production of graphite oxide is the same for all these methods, the graphite starting material is exposed to a mixture of strong acids and oxidising agents. This introduces a wide range of oxygen functionalities including but not limited to alcohol, carboxylic acid and epoxide functional groups.\textsuperscript{46} The most commonly accepted model for graphite oxide was proposed by Lerf and Klinowski in 1998 (Figure 2.1.9), following experiments using C\textsuperscript{13} and H\textsuperscript{1} nuclear magnetic resonance (NMR).\textsuperscript{47} The model shows the wide range of functional groups in random locations with no visible patterns in the structure. This random amorphous structure is comprised of both sp\textsuperscript{2} and sp\textsuperscript{3} carbon atoms, as the oxidation process changes the sp\textsuperscript{2} carbon atoms of graphite into sp\textsuperscript{3}. These new sp\textsuperscript{3} atoms, coupled with the oxygen functional groups, disrupt the van der Waals interactions allowing flakes to be easily exfoliated and remain stable in aqueous solution via mild sonication. The Hansen solubility parameters for GO are given as $\delta_D \sim 17.5 \text{ MPa}^{\frac{1}{2}}$, $\delta_p \sim 10 \text{ MPa}^{\frac{1}{2}}$ and $\delta_H \sim 15.7 \text{ MPa}^{\frac{1}{2}}$ resulting in a Hildebrand solubility parameter of $\delta_T \sim 25.4 \text{ MPa}^{\frac{1}{2}}$.\textsuperscript{48} The oxygen functionality present in GO is responsible for an increase in hydrogen bonding between GO sheets and water, therefore increasing $\delta_H$ in particular when compared with graphene.
However, the introduction of sp$^3$ carbon atoms into the lattice structure also disrupts the conjugated delocalised $\pi$ bonding which is responsible for electrical conduction. Therefore, graphite oxide does not share the same two dimensional electrical conduction properties of graphite. Rather, the electrical properties of graphite oxide are dependent on the amount of oxidation present. If all the carbon atoms were converted into sp$^3$ atoms, there would be no $\pi$ bonding molecular orbitals, making the band gap the same as the difference between the $\sigma$ and $\sigma^*$ C - C bonds. This is characteristically a very large band gap and therefore, the material would be an insulator, with similar electrical properties to diamond. Conversely, in a less oxidised variation of graphite oxide, most of the sp$^2$ carbon network remains intact, and therefore the band gap would remain small. In this case, the material would be classed as semi conducting. It is also calculated that the work function of GO and rGO materials are dependent on their oxygen content and the type of oxygen functional groups present, as shown in Figure 2.1.10. Therefore, it is important to gauge the degree of oxidation present in a graphite oxide sample, as it will have ramifications on the electrical properties of both the parent graphite oxide and the exfoliated GO.
Owing to the reduction in Van der Waals interactions for graphite oxide when compared with graphite, it is possible to exfoliate single layer GO sheets via sonication. In the process of sonication, ultra-sonic frequency sound waves are applied to a solution, forming temporary microscopic bubbles which release energy when they collapse, which in turn agitates material particles. This agitation causes separation of the layers of graphite oxide, but has also been shown to break down the lateral size of flakes. Studies using atomic force microscopy (AFM) have shown that the oxidation of graphite and subsequent sonication of graphite oxide can produce a majority of monolayer flakes, with an average flake thickness of 1.4 nm. The flake thickness will vary depending on both the amount of sp$^3$ carbon atoms, which causes bends in the flat sp$^2$ sheet, and on the oxygen functionality on the flake surface. These factors, coupled with wrinkles often found when measuring flakes results in a variation of flakes thicknesses being reported in the literature, with a
range of average flake thicknesses reported from 1.0 nm\textsuperscript{40} to approximately 1.75 nm\textsuperscript{46}. High resolution transmission electron microscopy images comparing graphene GO and rGO show distinct regions of both sp\textsuperscript{3} disorder and graphitic sp\textsuperscript{2} ordered clusters on the surface (Figure 2.1.11).

As a result of GO's less favourable electronic properties, it is not used directly in many electrical applications. It has however been shown to be useful in some applications, including bio-sensing\textsuperscript{54} and as a surfactant for other insoluble materials\textsuperscript{55}. It can also be used as a thin film electronic charge transport material in OPV. This will be examined in more detail in Section 2.2.4. However, by far its most common use is as an intermediate in the production of rGO a chemically synthesised graphene like material.

2.1.4 Reduction of Graphene Oxide

The reduction of GO to produce graphene was envisioned as a simple cost effective method of producing large quantities of solution process-able graphene material. However, the material produced by GO reduction was shown to still contain some oxygen functionality, as well as defects in the lattice structure\textsuperscript{56}. It cannot be considered the same as pure graphene.
and is therefore called rGO. Owing to the wide variety of reducing agents, which allow for reduction of GO in different ways, the label rGO covers a wide range of materials with similar properties.

As previously discussed, the addition of oxygen functionality introduces sp\(^3\) carbon atoms into the graphene lattice, which in turns limits GO’s conductivity. In an ideal reduction, all these sp\(^3\) atoms would be converted back to sp\(^2\) carbon atoms and the ballistic conductivity of graphene would be restored. However, in most cases, the aggressive removal of oxygen functionality leaves defects in the lattice structure.\(^57\) These defects are detectable using a technique called Raman spectroscopy, which will be explained in more detail in Section 2.3.1. These defects, coupled with unreduced oxygen functional groups, leads to the lower conductivity of individual rGO flakes compared to pristine graphene sheets.\(^58\) Furthermore, most conductivity measurements are taken as thin film measurements which are also affected by flake to flake charge transfer transitions. These flake to flake transitions will potentially limit the conductivity of rGO thin films, through the addition of multiple junction electrical resistances.

In the literature, there are many different methods of reducing GO to rGO.\(^56\) The simplest of these reduction methods is thermal annealing. The exact mechanisms of how GO is thermally reduced are unclear; however, investigations using X-ray photoelectron spectroscopy (XPS) have provided an estimation of the concentration of oxygen containing functional groups remaining after thermal annealing.\(^59\) These investigations (Figure 2.1.12) show a decrease in C – O – C and C = O concentration with increasing temperature, while the concentration of C – OH functional groups first increases then decreases after 400\(^\circ\)C. This initial increase in concentration is explained by the formation of phenolic groups at the expense of C – O – C functional groups.\(^59\) The thermal reduction of GO is a useful method for producing rGO on a substrate surface, as it limits any adverse effects caused by aggregation in solution; however, the high temperatures required in the reduction (+400\(^\circ\)C) can make it less favourable when compared with low-temperature chemical reduction methods.
The most common chemical reduction method uses hydrazine (N$_2$H$_4$) as a reducing agent. Due to the large number of varying functional groups present on GO, it is difficult to determine which functional groups are affected by the hydrazine reduction. Suggested reduction mechanisms for hydrazine can be found in literature. These mechanisms suggest that hydrazine removes epoxide groups on the surface of GO sheets, as well as forming hydrazone groups by reacting with carbonyl groups. Using a density functional theory method, the effect of hydrazine and thermal reduction on oxygen containing functional groups has been theoretically determined in the literature (Table 2.1-1). The theoretical results predict that epoxide and alcohol groups in the centre of the flakes should be removed by hydrazine reduction.

\[
\begin{array}{|c|c|c|c|}
\hline
\text{Oxygen Containing Functional Group} & \text{Hydrazine at Room Temperature} & \text{Thermal Treatment (700-1200°C)} & \text{Combined Hydrazine and Thermal Treatment} \\
\hline
\text{Epoxide (C – O – C)} & \text{Removed} & \text{Not Removed} & \text{Removed} \\
\text{Edge Epoxide (C – O – C)} & \text{Converted}^a & \text{Not Removed} & \text{Not Removed} \\
\text{Alcohol (C – OH)} & \text{Removed} & \text{Removed} & \text{Removed} \\
\text{Edge Alcohol (C – OH)} & \text{Not Removed} & \text{Removed} & \text{Removed} \\
\text{Carboxyl (C = O)} & \text{Not Removed}^b & \text{Not Removed} & \text{Not Removed} \\
\text{Carboxylic acid (O = C – OH)} & \text{Partially Removed} & \text{Removed} & \text{Removed} \\
\hline
\end{array}
\]

* Converted into Hydrazino-alcohol * Literature calculations did not include the conversion of carboxyl groups into hydrazone groups, therefore may be converted instead of not removed.

As the hydrazine reduction can be completed at room temperature, it is much more favourable than thermal annealing when considering certain potential applications, for example integration with low melting point plastic materials as desired for flexible electronics. Additionally, the hydrazine reduction can be achieved in vapour form, allowing...
for the reduction of thin films after deposition.\textsuperscript{61} This eliminates the complications that arise from aggregation in solution. However, hydrazine reduction does have its disadvantages; for example, the introduction of hydrazone groups introduces nitrogen moieties into the graphene structure which may have adverse effects on the structural, chemical and electrical properties of the final material. The most important disadvantage of hydrazine reduction of GO is the use of hydrazine itself, as it is highly toxic and very flammable. This makes hydrazine reduction a less favourable option at an industrial level when compared with other options, despite it being the most studied, and therefore most understood, method.

One of the most interesting alternatives to hydrazine is ascorbic acid, also more commonly known as vitamin C. It is demonstrated that vitamin C reduction of GO can reach the same degrees of conductivity as hydrazine reduction, producing materials that are similar when examined using ultra violet – visible spectroscopy (UV-Vis) and thermogravimetric analysis (TGA).\textsuperscript{62} A detailed explanation of each of these techniques can be found in Section 2.3.4 and Section 2.3.2 respectively. The reduction of GO using vitamin C is very promising, as it uses a non-toxic environmentally friendly chemical which is naturally occurring. The reduction mechanism commonly proposed in the literature is presented in Figure 2.1.\textsuperscript{63} Similar to the mechanism for hydrazine reduction, the vitamin C reduction targets the epoxide functional groups. However, unlike hydrazine reduction vitamin C cannot introduce hydrazone groups or any other nitrogen containing moieties into the rGO structure.
Literature sources claim it is possible to produce stable suspensions of vitamin C rGO in aqueous solution at 0.1 mg/mL. It is speculated that the decomposition products of the used vitamin C act as a surfactant to limit the formation of agglomerates in the sample.\textsuperscript{64} It is also possible that the reduction was only partially completed, leaving enough oxygen functionality to keep the sheets from agglomerating. One of the most interesting developments regarding the reduction of GO is the use of sheet agglomeration to create microporous sponges.\textsuperscript{18} This will be explained in more detail in Section 2.2.4. The mechanism for rGO sponge formation is not fully understood at present, although it is clear that the transition of hydrophilic GO to hydrophobic rGO plays a vital role in the self-assembly process. Since the GO sheets are randomly orientated in solution, when reduction occurs the agglomerates are also randomly orientated, leaving the material porous. This is important as it ensures a large surface area, which is essential for absorbent material applications. This large surface area provides a useful 3D framework which could be exploited with additional functionalization to tailor properties to suit specific applications.

2.1.5 Functionalization of Graphene Oxide Materials

While GO and rGO materials exhibit a range of useful intrinsic properties, the wide range of varying functional groups and the amorphous nature of the materials offer many additional sites which can be used for functionalization. These functionalizations can provide enhancements to existing properties or add new properties not possible in the pristine
material. Varying types of functionalization are demonstrated in the literature on both the standard GO and rGO materials and on rGO sponges. Furthermore, the functionalizations range from covalent attachment of various chemical functional groups and polymers, non-covalent stacking or wrapping mechanisms, to decoration or implantation of metallic nanoparticles. This review section will focus primarily on the functionalization of GO, rGO and rGO sponges with metal nanoparticles.

One of the interesting properties that can be tailored with the incorporation of metal nanoparticles is the work function of GO materials for tuneable charge transport layers. The energy level alignment in charge transport materials is very important for electronic device applications, for example, in OPV which will be explained in more detail in Section 2.2.2. Through the addition of gold chloride (AuCl₃), an increase of work function from 4.42 eV to 5.12 eV was demonstrated for CVD grown multi-layer graphene. This increase in work function (or p-type doping) suits the hole transporting layer properties required in OPV as the polymers used typically have HOMO levels below 5 eV.

Another outcome from functionalization is the development of new properties not found in the intrinsic graphene based material. An example of this is introduction of magnetite (Fe₃O₄) nanoparticles onto the surface of rGO for use in arsenic removal. The addition of the magnetite nanoparticles onto the surface of the rGO sheets result in magnetic properties as demonstrated in Figure 2.1.14. The material demonstrates a magnetic coersivity (Hₓ) of approximately 12-20 Oe and a saturation magnetism (Mₛ) of 20-60 emu/g. Most importantly, the presence of the iron oxide nanoparticles gives the material a high magnetic susceptibility allowing for it to be pulled from solution through the application of an external magnetic field.
Another property which can be introduced by the addition of metal nanoparticles is antibacterial properties, which is of particular importance for water filtration applications, for example, it is well documented that silver nanoparticles can be antimicrobial and antibacterial.\textsuperscript{68,69} These silver nanoparticles are typically synthesised using silver nitrate combined with a reducing agent. The literature details various methods of reducing GO and silver nitrate in situ to produce antibacterial GO-Ag hybrid materials.\textsuperscript{69} By combining this with breakthroughs creating GO sponges/hydrogels, it was demonstrated that a GO-Ag sponge can effectively filter \textit{E. coli} from contaminated water (Figure 2.1.15).\textsuperscript{70}
2.2 Applications

2.2.1 Overview

The many favourable properties of graphene materials have led to numerous attempts to use it in various applications. Due to its promising electrical properties and near optical transparency, one of the most desired goals is the use of graphene materials in transparent conducting electrodes, as a gateway material towards flexible electronics. Significant research interest is invested in the use of rGO materials as a transparent electrode, for the more favourable solution properties would allow for the creation of graphene based ink, which could be used in the mass production of flexible electronic applications. This application will be detailed further in Section 2.2.2.

However, as previously discussed in Section 2.1.4, rGO is often limited by the aggregation that occurs as oxygen functionality is removed. Alternatively, solution processable GO materials can be used in some applications. One of the possible applications for GO materials is for use in water desalination, as the GO membranes demonstrate that they allow water to flow through, while stopping ions and larger molecules from traversing (Figure 2.2.1).\(^{71}\) Owing to GOs less favourable electronic properties, there are not many

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**FIGURE 2.1.15 E. COLI CELL COLONIES IN WATER SAMPLES, (A) UNFILTERED, (B) rGO SPONGE FILTERED, AND (C) Ag/rGO FILTERED. (D) E. COLI INACTIVATION RATES ACHIEVED BY rGO HYDROGEL AND Ag/rGO HYDROGEL AT DIFFERENT INITIAL E. COLI CONCENTRATIONS (REPRINTED WITH PERMISSION FROM REF 70. COPYRIGHT 2015 JOHN WILEY AND SONS.)**
applications that use GO in electrical applications. Thin films of GO have been used in OPV devices as effective charge transport layers which will be explained further in Section 2.2.4.

![Diagram](image)

**FIGURE 2.2.1 SCHEMATIC DIAGRAM INDICATING THE SEPARATION MECHANISM OF THE FREESTANDING GRAPHENE AND GO MEMBRANES FOR WATER DESALINATION. (REPRINTED WITH PERMISSION FROM REF 71. COPYRIGHT 2015 ELSEVIER B.V.)**

Owing to its useful electrical properties, rGO has many other potential applications, including as platforms for biosensors, energy storage, and supercapacitors. Many of these applications benefit from materials with large surface areas, such as the rGO microporous sponges. The high surface area of the rGO sponges also makes them useful as absorbent materials, which will be discussed further in Section 2.2.5.

Many of the other properties of graphene materials lead to interesting potential applications. For example, the lightweight nature of graphene coupled with its strength are hoped to be utilised in the development of strong lightweight hybrid composite materials, which could be used in aircraft, where additional weight lowers fuel efficiency. The addition of functionalised graphene materials could lead to countless more possible applications and therefore, only a select few applications will be discussed in further detail in the following sections.

2.2.2 TRANSPARENT CONDUCTING ELECTRODES
The most researched application for graphene use is as a transparent conducting electrode. This utilises the remarkable electrical properties and optical transparency of graphene as an electrode for electrical devices. Transparent conducting electrodes allow for semi-transparent electronics, as well as playing a vital role in optical electronics. Currently, the most common material used as a transparent conducting electrode is indium tin oxide (ITO). However, ITO has its disadvantages, for example, the scarcity of indium as a metal, which
leads to the continuously increasing price of ITO based devices.\textsuperscript{72} Another key disadvantage of ITO as a material is that it is brittle, which greatly limits the flexibility of possible plastic electronic devices. It has also been showed that indium ions can diffuse out of the ITO structure into devices under acidic conditions which greatly increases the chance of device failure.\textsuperscript{73,74} Therefore, a suitable replacement for ITO is highly sought after. Various carbon nano-material alternatives have been demonstrated as being able to reach similar low sheet resistances to ITO without sacrificing transparency. Commercially available ITO substrates have a sheet resistance as low as 10 $\Omega/\square$ while maintaining 83\% light transmission in the visible light region. Using CVD grown graphene it has been shown that graphene can reach 30 $\Omega/\square$ at approximately 90\% transmission.\textsuperscript{75}

Sheet resistance is the typical measure of resistance in thin films, which is defined as the resistance across a square shaped thin film of any size dimensions. Resistance is defined as,

$$R = \rho \frac{L}{W \times t}$$ \hspace{1cm} (Equation 2)

where $\rho$ is the resistivity of the material, $L$ is the length of the material, $W$ is the width of the material and $t$ is the thickness of the material. Sheet resistance ($R_s$) can also be defined as,

$$R_s = \frac{\rho}{t}$$ \hspace{1cm} (Equation 3)

Therefore, by combining Equations 2 and 3 the resistance of a thin film can be measured as,

$$R = R_s \frac{L}{W}$$ \hspace{1cm} (Equation 4)

This leads to the measuring of resistance for a series of known path lengths with electrodes of a set width, making it possible to measure the sheet resistance. This method is called transmission line measurements (TLM). The sheet resistance of thin films is highly dependent on the thickness of the material. This is best explained by considering the difference between series and parallel circuits (Figure 2.2). In a circuit where all the resistors are linked in a chain, the total resistance associated with the series circuit ($R_{\text{se}}$) is the sum of all the individual resistors,
However, for a parallel circuit, where resistors are connected in parallel, the total resistance ($R_p$) is defined as

\[
R_p = \left( \frac{1}{R_1} + \frac{1}{R_2} + \frac{1}{R_3} + \cdots + \frac{1}{R_n} \right)^{-1}
\]

(Equation 6)

This means that in a series circuit, such as laterally through a series of graphene type layers, the resistance is determined by the sum resistance of each layer. In contrast, in a parallel circuit, such as a sheet resistance measurement with a set thickness, each parallel circuit contributes to lowering the resistance. Therefore, the sheet resistance can be decreased by increasing the thickness of the thin film. For transparent conductors, this creates a trade-off, as increasing thickness increases the optical absorption, making it less transparent. This makes sheet resistances only comparable with their respective thicknesses or optical transmission properties.

A suggested figure of merit used to measure transparent conducting electrodes is to calculate the $\sigma_{\text{DC}}/\sigma_{\text{Op}}$ value for the transparent conducting material. The 3D DC conductivity ($\sigma_{\text{DC}}$) is the inverse of the resistivity for the material which can be worked out from the sheet resistance,

\[
R_s = (\sigma_{\text{DC}} \cdot t)^{-1}
\]

(Equation 7)

The optical conductivity ($\sigma_{\text{Op}}$) is a measure of the optical properties, which can be determined from the optical transmission ($T_{\text{Op}}$),
where \( Z_0 \) is the impedance of free space (ca. 377 \( \Omega \)). By combining Equations 7 and 8, it is possible to remove the dependence of the thickness of the film (\( t \)), leaving \( \sigma_{DC}/\sigma_{Op} \) which can be calculated from the sheet resistance and transmission of the film.

\[
\frac{\sigma_{DC}}{\sigma_{Op}} = \frac{Z_0}{2R_s(T_{Op}^{\frac{1}{2}} - 1)} \quad (Equation \ 9)
\]

This ratio can be used as a figure of merit to compare thin film samples regardless of thickness. It is suggested that to be competitive with ITO the material would require a value of 30.\(^{76}\)

However, as previously discussed, solution process-ability is also an important attribute in the development of cheap mass producible electronic devices. Neither ITO deposition nor CVD graphene growth is considered a solution processable method, and so alternatives are still under development. Reduced GO represents an interesting potential material for this application (Figure 2.2.3); however the resistance of rGO films is not low enough to be a viable alternative to ITO at present.\(^{61}\) It is suggested that the \( \sigma_{DC}/\sigma_{Op} \) ratio for solution based graphene network is limited to 0.7; limited by the probability of electrons tunnelling through overlapping flakes. However, one of the lowest reported sheet resistance values for rGO thin films is \( 2.2 \times 10^3 \, \Omega/\square \) at 84\% transmission, which was achieved by spray coating a GO and hydrazine mixture onto a substrate preheated to 240\(^{\circ}\)C.\(^{77}\) This equates to a figure of merit value of 0.98 which suggests that there may be ways of surpassing this limit. One of the highest values for \( \sigma_{DC}/\sigma_{Op} \) is achieved for an rGO film annealed at 1100\(^{\circ}\)C with a value of 1.6.\(^{52}\)
Figure 2.2.3 Sheet resistance and transmission measurements for graphene oxide thin films, reduced using hydrazine and thermal annealing (550°C). (Reprinted with permission from Ref 61. Copyright 2008 Macmillan Publishing Group)

2.2.3 Conduction Mechanisms
Understanding the mechanisms for electrical conduction is important for optimisation of charge transporting materials. Typically, conduction mechanisms can be categorized as either low field (< $10^6$ Vcm$^{-1}$) or high field (> $10^6$ Vcm$^{-1}$). Field strength ($E$) across a device can be determined using the following:

$$E = \frac{V}{d}$$

Equation 10
where $V$ is the applied voltage, and $d$ is the distance between the contacts. In thin film devices, the distance between the contacts are typically only a few hundred nanometres, meaning that a high field is being generated. The conduction mechanisms that occur in the high field region are space charge limited current (SCLC), the Poole Frenkel effect (PF), the Schottky effect (Sch), and Tunnelling effects such as Fowler Nordheim Tunnelling (FN).

SCLC is considered the simplest conduction mechanism, and takes place when one charge carrier is more mobile than the other. This results in conduction being limited by the mobility of the slowest carrier, and therefore SCLC is considered a bulk limiting conduction mechanism, as opposed to an interface limiting mechanism. In the simplest case, where there are no traps (i.e. impurities) are present to stop charge carriers, electrical conduction is defined by the Mott–Gurney equation,\(^7\)

$$J = \frac{9}{8} \mu \varepsilon_f \varepsilon_0 \frac{V^2}{L^3}$$ \hspace{1cm} \text{Equation 11}

Where $J$ is current density, $\mu$ is the free carrier mobility, $\varepsilon_r$ and $\varepsilon_0$ are the relative permittivity and permittivity of a free space respectively, $V$ is the applied voltage and $L$ is the length between the electrodes. This leads to a current to voltage relationship of $J \propto V^2$ when no traps are present. However, when traps are present it is shown that,\(^7\)

$$J = N_c \mu e \alpha^{l-1} \left( \frac{e l}{N_c (l + 1)} \right)^l \left( \frac{2l + 1}{l + 1} \right)^{l+1} \frac{V^{l+1}}{L^{2l+1}}$$ \hspace{1cm} \text{Equation 12}

where $N_c$ describes the number of energy states of the valence band, $N_t$ describes the total number of traps, $e$ is the elementary charge ($1.602 \times 10^{-19}$ Js), and $l$ describes the trap distribution. This can be simplified to give a current voltage relationship of $J \propto V^{l+1}$. This leads to a current voltage response similar to the schematic shown in Figure 2.2.4 which can be described in 4 distinct regions.\(^8\)
The first region (A) in Figure 2.2.4 is the Ohmic region, which occurs at low voltages, and where \( J \propto V \) as defined by Ohms law (\( V = IR \), where \( R \) is the electrical resistance). At higher voltages (region B), SCLC behaviour manifests with charge carriers falling into potential energy wells (also termed traps) in the material, leading to a current voltage relationship of \( J \propto V^{l+1} \). In the case of a system with no traps present, i.e. \( l = 1 \), this is defined by the Mott–Gurney equation\(^{81,82}\) as shown by the blue line. As the voltage is increased further all the traps are filled, known as the trap fill limit (\( V_{\text{TFL}} \)), and \( J \propto V^n \) (C), until the current reverts to \( J \propto V^2 \) at D, where the conduction is carrier dominated and no longer affected by the traps present. Current-voltage analysis has shown that various polymer films including the OPV device architecture discussed in Section 2.2.3, conduct charge carriers according to the SCLC model.\(^{83}\)

The Poole- Frenkel effect is also a bulk limiting effect, caused by the removal of an electron from the material which in turn leaves a bound positive charge. This positive charge leads to the creation of a potential energy well in the bulk of the material.\(^{84}\) The PF effect is a high field effect, because a high field is required to remove the charge carrier from the potential well. This is depicted in Figure 2.2.5.

**FIGURE 2.2.4 CURRENT VOLTAGE ANALYSIS FOR A MATERIAL WITH TRAPS WHERE I DESCRIBES THE TRAP DISTRIBUTION, THE DASHED BLUE LINE REPRESENTS A MATERIAL WITH NO TRAPS (J \( \propto V^2 \)).**
At high fields, the Poole-Frenkel effect gives rise to a current dependent on the following equation,\(^8\)

\[
J = e\mu n_0 E \exp \left( -\frac{\phi_w - e\beta_{PF} E^{1/2}}{kT} \right) \quad \text{Equation 13}
\]

where

\[
\beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{1/2}
\]

and \(n_0\) is the number of free carriers, \(\phi_w\) is the barrier height, \(k\) is the Boltzmann constant \((1.38 \times 10^{-23} \text{ JK}^{-1})\) and \(T\) is the temperature in kelvin. Due to the high field contribution to this equation, the constant pre-terms \((e\mu n_0)\) are rendered insignificant and therefore, by plotting \(\ln(J/E) vs E^{1/2}\), it is possible to estimate the barrier heights of the potential well, and the relative permittivity of the material system. The full derivation and dimensional analysis of this equation is given in the appendices (Appendix 10.5).

Similar to the Poole Frenkel effect, the Schottky effect deals with the lowering of a potential barrier by an applied electric field. However, while PF is a bulk limiting effect, the Schottky effect occurs at the electrode interface, and is therefore classified as an electrode limiting mechanism.
At high fields this leads to a current relationship very similar to PF described as,\textsuperscript{24}

\[ J = A^{**}T^2 \exp\left(-\frac{\phi_w - e\beta_{Sch}E^{1/2}}{kT}\right) \]  \hspace{1cm} \text{Equation 14}

where

\[ \beta_{Sch} = \left(\frac{e}{4\pi\epsilon_0\epsilon_r}\right)^{1/2} \]

and \( A^{**} \) is the modified Richardson constant. Again, because of the high field contributions, the constant pre-term \((A^{**})\) are rendered insignificant and therefore it is possible to estimate the barrier height and relative permittivity of the material by plotting \( \ln(J/T^2) \) vs \( E^{1/2} \).

At high fields, it is possible to thin potential barriers to such an extent that carriers can quantum mechanically tunnel through the barrier. This is called Fowler-Nordheim tunnelling,\textsuperscript{86} which can be described using the following,\textsuperscript{87}

\[ I \propto E^2 \exp\left(-\frac{\kappa}{E}\right) \]  \hspace{1cm} \text{Equation 15}

where

\[ \kappa = \frac{8\pi(2m^*)^{1/2}}{3eh}\phi^3 \]

and \( m^* \) is the effective mass of a charge carrier and \( h \) is Planck’s constant (= 6.626x10^{-34} \text{ J.s})
Using this equation it is possible to estimate the tunnelling probability (κ) and from that the barrier height for a FN tunnelling system, allowing for comparison with expected barrier height values estimated from a band-gap diagram. All four of the high field conduction mechanisms allow for comparison with expected energy level values (measured using experimental techniques) which can be used to qualify which mechanism is most dominant in a specific device system.

2.2.4 ORGANIC PHOTOVOLTAICS

**BACKGROUND**

The photovoltaic effect is a term used for the direct conversion of light into electricity in semi-conducting materials. This is achieved by raising electrons from the band of occupied molecular orbitals (known as the valance band) to the band of unoccupied orbitals (known as the conduction band) by excitation with light. As previously discussed in Section 2.1.1, the difference between the HOMO and LUMO levels, (known as the band gap) corresponds to a particular energy which if applied can excite electrons from the HOMO level to the LUMO level. According to the Planck-Einstein relation, the energy of a photon of light is directly proportional to the frequency of the light. Therefore, because the frequency of light can be expressed as the speed of light divided by the wavelength, the energy of a photon is inversely proportional to the wavelength of the light. This means that if a semi conducting material with a specific band gap is illuminated by light of corresponding wavelength, an electron will be promoted from the valance band to the conduction band (Figure 2.2.8).
Once an electron is promoted from the valance band to the conduction band, it leaves a vacancy in the valance band known as an electron hole, colloquially termed a hole. Unless this electron-hole pair (commonly known as an exciton) is separated, the electron will relax, losing energy in the form of heat and recombining with the vacant hole. The excitation and relaxation of electrons is very important for a number of different vibrational spectroscopy methods, however the relaxation of electrons from the conduction band effectively lowers the number of charge carriers, lowering electrical conduction.

Therefore, in photovoltaic devices, electrons and holes are separated to avoid charge recombination. This is accomplished through the alignment of material energy levels which allows for quick extraction of charges into separate materials. For OPV, this involves matching energy levels of various conductive carbon based polymers and organic small molecules. In a basic single layer OPV device, this is achieved by applying electrodes to the light absorbing layer (also known as the active layer), where the work functions of the electrodes are similar to the HOMO and LUMO levels of the light absorbing layer. This enables electrons and holes to be extracted to separate electrodes before recombination occurs. This was greatly improved by the development of active layer combinations, which mixed light absorbing (electron donating) polymers with charge transfer (electron acceptor) molecules, to facilitate charge transfer which quickly separates the excitons. The simplest of these is the bilayer OPV, which utilises two layers of electron donor and acceptor next to
each other. A common example of a donor-acceptor combination for bilayer OPV is Poly(p-phenylene vinylene) (PPV) and C₆₀ as shown in Figure 2.2.9.

![Diagram of PPV and C₆₀](image)

_Figure 2.2.9 (a) Illustration of photoinduced charge transfer between PPV and C₆₀ with (b) a corresponding energy level diagram. After excitation in the PPV polymer, the electron is transferred to the C₆₀. The corresponding hole remains on the PPV. (Reprinted with permission from Ref 89. Copyright 2007 American Chemical Society.)

However, the probability of recombination increases depending on the distance the exciton has to travel to the electrode or the donor-acceptor interface. Typically, the exciton diffusion length is limited to 10 nm for the organic semi-conducting polymers used in OPV.⁹⁰ Therefore, in single layer and bilayer OPV devices, the optimal active layer thickness is only 10 - 20 nm, which is technically challenging and means only a small fraction of the incoming light can be absorbed. A solution to this problem is the development of the bulk heterojunction, where donor and acceptor polymers are blended together, leading to donor acceptor interfaces throughout the active layer as the materials separate into domains when processed. This allows for active layer thicknesses to be increased without increasing the distance excitons must travel to reach an interface. The single layer, bi-layer and bulk heterojunction active layer structures are visually represented in Figure 2.2.10.
With the absorption of photons and separation of the excitons optimised, the next step is to ensure that the charge carriers do not recombine upon reaching one of the electrodes. This is achieved by adding charge transport layers, more specifically, separate electron and hole transport layers. These interfacial layers assist in charge extraction by providing intermediate steps between the energy levels of the active layer and the Fermi level of the metal electrodes. This helps to lower the energy barrier at the electrode, assisting charge extraction in the direction dictated by the internal electric field. The most commonly used hole transport layer material is a blend of poly(3,4-ethylenedioxythiophene) and polystyrene sulfonate known commercially as PEDOT:PSS. PEDOT:PSS has a reported work function of 4.9 – 5.2 eV,\textsuperscript{91,92} making it a useful for OPV donor materials which typically have HOMO levels ranging from 4.8 – 5.5 eV.\textsuperscript{93}

**Measurement**

For a material to be useful as a hole transport layer, it should improve the efficiency of OPV devices in some way. OPV efficiency is measured based on three solar cell output parameters, the open circuit voltage ($V_{oc}$), the short circuit current density ($J_{sc}$) and the fill factor (FF). Consider a diode, where the current is dependent on the applied voltage and there is an equilibrium of charge carrier concentrations, this dependence can be expressed as,

$$I = I_0 \left[ \exp \left( \frac{eV}{nKT} \right) - 1 \right]$$  \hspace{1cm} \textit{Equation 16}

Where, $I$ is the current flowing through the diode, $I_0$ is the reverse saturation current, $V$ is the applied voltage and $n$ is an ideality factor ($n = 1$ in an ideal diode). This dependence defines the dark current properties of the device, which is the current generated when the voltage is swept without light present. Under illuminated conditions, excitons are generated
and are separated by the build in electric field to the electrodes, creating a photocurrent ($I_L$) in the opposite direction,

$$I = I_0 \left[ \exp \left( \frac{eV}{nkT} \right) - 1 \right] - I_L$$  \hspace{1cm} \textit{Equation 17}

Where $e$ is the elementary charge. At a high enough voltage, the reserve photocurrent counter acts the forward diode current, resulting in zero current. This is called the open circuit voltage, and can be derived from the equation by setting $I = 0$ as follows,

$$V_{oc} = \frac{nkT}{e} \ln \left[ \frac{I_L}{I_0} + 1 \right]$$  \hspace{1cm} \textit{Equation 18}

Similarly, by setting $V = 0$, the short circuit current ($I_{sc}$) can be determined,

$$I_{sc} = -I_L$$  \hspace{1cm} \textit{Equation 19}

The $I_{sc}$ can be converted into the $J_{sc}$ by factoring in the illuminated area of the device and therefore $J_{sc}$ is a measure of the photocurrent produced per unit area. Both the $J_{sc}$ and the $V_{oc}$ can be determined through measuring an I-V curve, in which the current generated is measured as the voltage is swept from 0 to $V_{oc}$. Given that power is defined as the product of current and voltage, in an ideal system ($\text{FF} = 100\%$), the maximum power ($P_{max}$) would be the product of the $J_{sc}$ and the $V_{oc}$. However, because of resistances within the device, a third PV output characteristic fill factor (FF) is used to describe the difference between $P_{max}$ and the $J_{sc} \times V_{oc}$ product,

$$FF = \frac{J_{MP} \times V_{MP}}{J_{sc} \times V_{oc}} = \frac{P_{max}}{J_{sc} \times V_{oc}}$$  \hspace{1cm} \textit{Equation 20}

Where $J_{MP}$ and $V_{MP}$ are the current density and voltage at maximum power respectively. The FF can therefore be used to describe the ‘squareness’ of the J-V curve as displayed in Figure 2.2.11. These output characteristics combined with the input power ($P_{in}$) can be used to determine the overall efficiency of the solar cell, the power conversion efficiency (PCE) where,

$$PCE = \frac{P_{max}}{P_{in}} = \frac{V_{oc} \times J_{sc} \times FF}{P_{in}}$$  \hspace{1cm} \textit{Equation 21}
The properties of the active layer material make a significant difference on the potential efficiency of OPV devices. Donor materials require deep HOMO levels to enlarge the difference between the HOMO level of the donor and the LUMO level of the acceptor. The size of this difference determines the measurable $V_{oc}$ in the final PV devices, as defined in Equation 22.

$V_{oc} \approx (1/e) \left( |E^{Donor\ HOMO}| - |E^{PCBM\ LUMO}| \right)$  \hspace{1cm} (Equation 22)

Therefore, device efficiency can be improved by using deep HOMO level materials. Another way to improve device efficiency is to lower the band gap of the donor material. This allows lower energy photons to cause excitation of electrons, allowing more charge carriers to be generated, increasing the current available for extraction. This is reflected in an increase in photocurrent produced and subsequently increased $J_{sc}$ values. Therefore, the careful selection of active layer materials can lead to increased PCE values as shown in Figure 2.2.12.
The most commonly researched photoactive OPV material is Poly(3-hexylthiophene) (P3HT) which is commonly blended with Poly(Phenyl-C₆₁-butyric acid methyl ester) (PC₆₀BM) as an acceptor material. With a HOMO level of 5.0 eV, P3HT can utilise a wide range of materials as charge transport layers. Using GO as a hole transport layer in a P3HT:PC₆₀BM OPV device, it is shown that it is possible to achieve efficiencies similar to the commonly used hole transport layer PEDOT:PSS in P3HT:PC₆₀BM OPV devices.

However, because the LUMO level of the PC₆₀BM acceptor material is approximately 4.3 eV, the high HOMO level of P3HT limits the V_{oc} of P3HT:PC₆₀BM OPV devices (V_{oc} ≈ 0.6 V), which subsequently restricts the final PCE. One of the most interesting new generation OPV active layer materials is the blend of Poly[N-9'-heptadecanyl-2,7-carbazole-alt-5,5-(4',7'-di-2-thienyl-2',1',3'-benzothiadiazole)] commonly known as PCDTBT and Poly(Phenyl-C₇₁-butyric acid methyl ester) or PC₇₁BM. With a HOMO level reported between −5.35 and 5.50 eV,²⁴,⁹⁵ PCDTBT has a much lower HOMO level, which allows PCDTBT:PC₇₁BM to reach V_{oc} values of approximately 0.8 - 0.9V. The band diagram of the PCDTBT:PC₇₁BM blend is shown in Figure 2.2.13.
LIFETIME

Another significant advantage of PCDTBT as an active layer material is the chemical stability of the polymer material. This has allowed PCDTBT devices to be fabricated in air via both an inkjet printing method and a spray coating method with minimal losses in efficiency.\textsuperscript{96,97} This makes PCDTBT a more promising candidate for scale up to large area devices.\textsuperscript{94} The chemical stability of PCDTBT also leads to an increase in device lifetime for encapsulated devices, after the initial burn in period seen in polymer solar cells. (Figure 2.2.14).\textsuperscript{98} Devices have been extrapolated to a lifetime of 6.2 years on average, in comparison to P3HT devices which are extrapolated to last for 3.1 years. It is noted that these devices are under constant illumination at one sun’s intensity, and assuming 5.5 hours of sun light at one sun intensity per day, 365 days a year. Therefore, the encapsulated PCDTBT devices tested exhibit a approximately 12500 working hours in total with PEDOT:PSS present.\textsuperscript{98} For GO devices to be considered as an alternative to PEDOT:PSS, GO devices will need to match or better the PEDOT:PSS devices for both efficiency and lifetime.
FIGURE 2.2.14 TYPICAL LIFETIME PROFILE FOR A STANDARD POLYMER SOLAR CELL WITH AN ORGANIC HTL AND A METAL CATHODE (Al/Ca) AND A COMPARISON OF DEVICE LIFETIMES FOR ENCAPSULATED P3HT AND PCDTBT DEVICES. (REPRINTED WITH PERMISSION FROM REF 98. COPYRIGHT 2011 JOHN WILEY AND SONS.)

However, due to the acidic nature of the sulfonate groups on the PSS polymer, devices made with PEDOT:PSS suffer from intrinsic lifetime issues. The acidity of PEDOT:PSS causes degradation of devices through the etching of indium from the ITO electrode which diffuses through the hole transport layer into the active layer. This effect was first observed in polymer light emitting diodes (PLED) using a technique called Rutherford back scattering (Figure 2.2.15).\(^73\) The acidic etching process is accelerated in ambient air conditions because PEDOT:PSS is hygroscopic, facilitating the adsorption of water which in turn speeds up the etching process.

FIGURE 2.2.15 (LEFT) DEPTH PROFILE OF INDIUM CONTENT IN A PLED DEVICE USING PEDOT:PSS, AFTER 48 HOURS EXPOSURE TO AIR, (RIGHT) INDIUM CONTENT IN THE PEDOT:PSS LAYER AS A FUNCTION OF EXPOSURE TIME TO AIR. (REPRINTED WITH PERMISSION FROM REF 73. COPYRIGHT 2000 APPLIED PHYSICS LETTERS)

Additionally, it is suggested that the presence of water causes an increase in series resistance in OPV devices. In brief, it is shown that the water creates electrically insulating
regions which causes an increase in series resistance, which consequently lowers the device’s fill factor (FF). The presence of insulating regions also lowers the potential current output, lowering the $J_{sc}$ and therefore the device efficiency.  

It was demonstrated that devices without a PEDOT:PSS layer last significantly longer in humid conditions (Figure 2.2.16). Therefore, it is important to look at alternatives to PEDOT:PSS to ensure fabricated devices are not limited by short device lifetimes.

**FIGURE 2.2.16 (TOP) NORMALISED PHOTOVOLTAIC PERFORMANCE CHARACTERISTICS AND (BOTTOM) SERIES RESISTANCES FOR AN UNENCAPSULATED MDMO-PPV:PCBM SOLAR CELL WITH AND WITHOUT A PEDOT:PSS LAYER, AS A FUNCTION OF EXPOSURE TIME TO A HUMID NITROGEN ATMOSPHERE (NITROGEN CONTAINING 0% OXYGEN, 40% RH) IN THE DARK. (REPRINTED WITH PERMISSION FROM REF 99. COPYRIGHT 2006 ELSEVIER.)**

**GRAPHENE OXIDE AS A HOLE TRANSPORT LAYER**

There are a few materials that can be used as an alternative to PEDOT:PSS in OPV devices. Various nanoparticle transition metal oxides, including nickel, vanadium and molybdenum oxide, have been demonstrated to have low enough work functions to be useful. However, deposition of these materials can prove difficult, often requiring evaporation
under vacuum conditions. Also the toxicity of some of these metals cannot be understated, making disposal of solar cells incorporating these metal oxides very expensive. Therefore, research into carbon based alternatives is on-going. Previously, it has been demonstrated that a solution processed ultra thin layer of GO (< 10 nm) can be used as a hole transport layer. With a reported work function ranging from 4.6 – 4.9 eV, GO has a work function close to some commonly used OPV materials.

The first literature source describing GO as a hole transport layer in OPV focused on P3HT:PC₆₀BM, as the maximum Vₜₜ is limited by the active layer blend rather than the effect of the GO HTL. It is demonstrated that the optimal layer covers the surface completely with the thinnest layer possible. Increases in the layer thickness maintained the Vₜₜ value, but were detrimental to Jₘₚ and FF. The Jₘₚ decrease is caused by an increased absorption with layer thickness for the GO layer, blocking light into the active layer. This can be confirmed by looking at the external quantum efficiency (EQE) which measures the amount of photons excited and electron-hole pairs extracted for each wavelength compared a set input intensity. It is possible to integrate the area under an EQE spectra to confirm the value of the Jₘₚ measured. The decrease in FF with increasing GO thickness is correlated to an increase in series resistance, which is caused by the insulating nature of the GO film.

Including results presented in this thesis, there are numerous examples of GO being used in various OPV systems as a hole transporting layer. A selection of these results are presented in Table 2.2-1. The device active areas are included for comparison, as the importance of active area will be discussed in Chapter 5.

<table>
<thead>
<tr>
<th>Device Architecture</th>
<th>PCE (%)</th>
<th>Comment</th>
<th>Active Area</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al/ETL/PCDTBT:PCBM/GO/ITO₀²⁴</td>
<td>5.0</td>
<td>See chapter 5 for more details</td>
<td>0.64 cm²</td>
</tr>
<tr>
<td>Al/ETL/PCDTBT:PCBM/PEDOT:PSS/ITO₀²⁴</td>
<td>5.3-6.0</td>
<td>See chapter 5 for more details</td>
<td>0.64 cm²</td>
</tr>
<tr>
<td>Al/GO/PCDTBT:PCBM/ETL/ITO₀²⁵</td>
<td>5.5</td>
<td>Inverted device</td>
<td>0.04 cm²</td>
</tr>
<tr>
<td>Al/P3HT:PCBM/GO/ITO₀²⁴</td>
<td>3.5</td>
<td>First Reported GO HTL</td>
<td>0.10 cm²</td>
</tr>
<tr>
<td>Al/P3HT:PCBM/GO/ITO₀²⁵</td>
<td>3.7-4.0</td>
<td>P3HT active layer/ annealed GO HTL (250°C - 350°C)</td>
<td>0.04 cm²</td>
</tr>
<tr>
<td>Al/P3HT:PCBM/PEDOT:PSS/ITO₀²⁶</td>
<td>3.8</td>
<td>P3HT active layer/ PEDOT:PSS HTL</td>
<td>0.04 cm²</td>
</tr>
<tr>
<td>Al/(Li)/PTB7:PCBM/GO/ITO₀²⁷</td>
<td>7.39</td>
<td>PTB7 active layer/ GO HTL</td>
<td>0.06 cm²</td>
</tr>
<tr>
<td>Al/(Li)/PTB7:PCBM/PEDOT:PSS/ITO₀²⁷</td>
<td>7.46</td>
<td>PTB7 active layer/ PEDOT:PSS HTL</td>
<td>0.06 cm²</td>
</tr>
<tr>
<td>Al/ETL/CH₃NH₃PbI₃,Cl₂,PCBM/GO/ITO₀²⁸</td>
<td>11.11</td>
<td>Perovskite</td>
<td>0.07 cm²</td>
</tr>
</tbody>
</table>
2.2.5 Sorbent Materials

The term ‘sorption’ can be defined as the process of attaching one substance to another. This is commonly divided into two subcategories, adsorption and absorption. Adsorption is the process of attaching the target substance (adsorbate) to the adsorbing surface (adsorbent), through chemical or physical adhesion. In chemical adsorption (chemisorption) a covalent bond is formed between the adsorbate and the adsorbent, while in physical adsorption (physisorption) the adsorbate is held in place via van der Waals interactions. The process of adsorption differs from absorption, which involves the incorporation of the target substance (absorbate) into the bulk of the absorbing material (absorbent). The difference between adsorption and absorption is often confused and is therefore visualised in Figure 2.2.17.

FIGURE 2.2.17 SCHEMATIC REPRESENTATION OF ADSORPTION AND ABSORPTION.

Adsorbent materials are used in a wide range of applications, including water filtration, energy storage and environmental remediation. To be a good adsorbent, materials with high surface areas are required, allowing for a large volume of adsorbate to be adsorbed onto the surface of the material. This generates a larger proportion of active sites to which the adsorbate molecules can bind, increasing the materials adsorption capacity. This high surface area can be achieved by creating a porous material, with a range of different pore sizes. Pore sizes are typically classified in 3 categories, macropores (>50nm), mesopores (50nm – 2nm), and micropores (<2nm). One of the most commonly used adsorbent materials is activated carbon, which is commonly used in water filters. It has been demonstrated that activated carbon has a high degree of micro-porosity allowing for the adsorption of a large amount of adsorbate. Activated carbon is a hydrophobic adsorbent material, and therefore is commonly used in the adsorption of organic substances or non-
polar adsorbates from water. Owing to the cheap method of production, activated carbon water filters are commercially available and very commonly used.

While the large surface area and cheap production methods make activated carbon a very useful material, it is not without its disadvantages. One such disadvantage is the high amount of energy required to synthesize it, with temperatures of 600 – 900°C required to pyrolysis the carbon precursors. Another major disadvantage with activated carbon water filters is that they can easily become a breeding ground for various bacteria. This is expedited by the removal of free chlorine ions from the water by the activated carbon filter. The primary mechanism for adsorption in activated carbon is understood to be physisorption as non-polar molecules are attracted to the 3D carbon matrix via van der Waals interactions.

The sorption of molecules onto an adsorbent material, whether through chemisorption or physisorption, can be kinetically described in three stages. Firstly, molecules from the liquid phase must diffuse into the adsorbent material, typically across a liquid film covering the adsorbent surface. Secondly, the molecules must diffuse through the adsorbent material itself, travelling along pore walls in a process known as intraparticle diffusion, until it reaches the final stage which involves the adsorption of the molecule into the adsorbent active site. Determining which of these stages is the rate determining step for the adsorption process is vital to ensuring the production of the highest quality adsorbents.

The process of intraparticle diffusion can be modelled using Weber’s pore diffusion model, which is expressed through the following equation,

\[ q_t = k_i t^{0.5} + c \]  

Where \( q \) is the amount adsorbed onto adsorbent, \( k \) is the intraparticle diffusion constant, and \( c \) is the intercept which is related to the resistance to transferring mass across the external liquid film. If this intercept can be extrapolated to zero it shows that the rate of adsorption is solely limited by intraparticle diffusion.

The process of adsorption onto the surface can also be modelled kinetically by investigating the order of the reaction. A typical adsorption reaction can be simplified into the following second order reaction equation.
\[ A + B \leftrightarrow AB \quad \text{Equation 24} \]

where \[ \text{Rate} = k[A][B] \]

and \( k \) is the rate constant, and \([A]\) and \([B]\) are the concentrations of reactants \( A \) and \( B \) respectively. This equation assumes that one molecule of \( A \) reacts with one molecule of \( B \). In the case of adsorbent materials this equates to one molecule of the adsorbate reacting with one adsorbent active site. However, in the case of a large adsorbent which can adsorb large amounts of molecules, or in a case where multiple molecules can be adsorbed onto a single active site (such as crystallisation of molecules on the surface) it is often easier to consider the rate equations based on a pseudo first order rate equation in which,

\[ \text{Rate} = k'[B] \quad \text{Equation 25} \]

where \[ k' = k[A] \]

and \( k' \) is the observed rate constant for the experiment. When applied to adsorption this leads to the pseudo first order kinetic model in which,\(^{113}\)

\[ C = C_0 e^{-k't} \quad \text{Equation 26} \]

where \( C \) is the concentration of the adsorbate at time, \( t \), and \( C_0 \) is the starting concentration of the adsorbate. Plotting \( \log(C) \) against \( t \) should result in a linear relationship, from which the rate constant can be calculated if this model holds. The pseudo first order rate equation can also be considered in terms of the amount of adsorbate adsorbed, in which,

\[ q_t = q_e \left(1 - e^{-k't} \right) \quad \text{Equation 27} \]

where \( q_e \) is the amount adsorbed at equilibrium. \( q_e \) acts as an indicator for the total number of active sites. This equation can be linearized to give the following,\(^{114}\)

\[ \log(q_t - q_e) = \log(q_e) - \frac{k't}{2.303} \quad \text{Equation 28} \]

which can be used to approximate the rate constant, by plotting \( \log(q_t - q_e) \) against time.

Another approximation commonly used when trying to understand the adsorption properties of carbon based materials is the pseudo second order kinetic model, where the
adsorbate molecule is assumed to adsorb onto two active sites. This can be represented kinetically as follows,\textsuperscript{113}

\[ C = \frac{C_0}{1 + k'' C_0 t} \quad \text{Equation 29} \]

where \( k'' \) is the pseudo second order rate constant. This model can also be expressed in terms of quantity of adsorbate adsorbed, which when linearized results in,\textsuperscript{114}

\[ \frac{t}{q_e} = \frac{1}{k'' q_e^2} + \frac{1}{q_e} t \quad \text{Equation 30} \]

which can be used to estimate both \( q_e \) and \( k'' \) by plotting \( t/q_e \) against time.

As previously mentioned in Section 2.1.4, rGO materials can be used to form a large surface area material which can be used in a similar manner to activated carbon with additional options for functionalization. It is theorised that the adsorption of organic materials onto rGO sponges occurs through van der Waals interactions similar to what applies for activated carbon. This allows rGO sponges to adsorb a wide variety of materials including oil and petroleum products, organic solvents and commercially used dyes.\textsuperscript{18} Industries such as textiles, cosmetics and paper use large quantities of dye which can greatly affect water quality if left untreated. One such dye pollutant molecule is the suspected carcinogenic, pink fluorescent dye Rhodamine B (RhB), which produces a strong peak in UV-Visible spectroscopy at 554nm.\textsuperscript{115} (Figure 2.2.18)

![Figure 2.2.18 Chemical Structure of Rhodamine B.](image_url)
2.3 INSTRUMENTATION

2.3.1 RAMAN SPECTROSCOPY

The most common technique for examining carbon materials, particularly graphene based materials is Raman spectroscopy. In essence, Raman spectroscopy is a vibrational spectroscopic technique, similar to Infrared spectroscopy which is examined in more detail in Section 3.3. Both techniques are highly selective, allowing for differentiation between separate chemical species. This makes both Raman and Infrared spectroscopy important analytical techniques for observing changes in molecular bond structure or molecular finger printing.

In Raman spectroscopy, a single wavelength of light is used to excite electrons from an energy level into a higher virtual excited state. After excitation, electrons relax to a lower energy level, emitting a photon with an energy corresponding to the energy difference. This gives rise to a variety of possibilities, described in Figure 2.3.1. The first possible outcome is that the electron will relax back to the same energy level that it was excited from. This is known as Rayleigh scattering, and results in no difference in energy between the excitation and relaxation. This lack of energy difference means that no change is observed between the emitted light and the input light. Therefore, Rayleigh scattering is not used in Raman spectroscopy, and so the energy of both the input light and Rayleigh scattering is filtered out.

![Energy Diagram](image)

*Figure 2.3.1 Energy diagram demonstrating the different types of scattering associated with Raman spectroscopy. An example of relaxed fluorescence is also shown.*

The next possible outcome is that the electron relaxes to an energy level higher than the energy level it was originally excited from. This is known as Stokes scattering, and results in an energy difference between excitation and relaxation equal to the difference in energy levels. Typically, the excitation in this case occurs from the ground level where the probability of finding an electron is highest. The third possibility, which involves an electron
relaxing to a lower energy level than its original energy level, is known as Anti-Stokes scattering. The signal produced by Anti-Stokes scattering is much smaller than that for Stokes scattering as the probability of finding an electron in the higher vibrational energy levels is much reduced. Consequently, the Stokes shift is more commonly used to examine the molecular structure.

The Raman scattering of molecules is dependent on the polarizability of the molecule. Polarizability can be defined as the ability for a molecule to form an induced dipole moment in an electric field. In essence, this can be described as a measure of how easy it is for the molecule’s electron cloud to be distorted by an external electric field, such as the electric field generated by interaction with laser light. The electric field generated by the Raman excitation laser distorts the electron cloud, allowing for the generation of separate vibrational energy levels which give rise to Stokes and Anti Stokes scattering.

One of the major problems that can occur with Raman spectroscopy is competition with a similar process known as fluorescence. This is where the excited electron has enough energy to reach an energy level above the LUMO level rather than the virtual level. In this instance, the electrons first relax to the LUMO level, through non radiative transitions, and then subsequently a photon is emitted as the electron relaxes back to the lower energy level. This two- step process takes longer than Raman scattering, taking nanoseconds rather than near instantaneous picoseconds. However, if fluorescence occurs, it is often more intense than the Raman scattering, leading to an obscuring of the Raman peaks in the spectra.

When looking at graphitic materials, the primary Raman active vibrational modes are the A\textsubscript{1g} and the E\textsubscript{2g} modes which are depicted in Figure 2.3.2. These two vibrational modes give rise to two important peaks in the Raman spectra, labelled the D and G bands respectively. The D band, which commonly is commonly found at around 1355 cm\textsuperscript{-1}, is produced by the breathing mode of six membered aromatic rings. In perfect graphite or graphene materials, this peak is not seen as the breathing mode is forbidden. The D band is only activated in the presence of disorder, either at defect sites or at the edges of sp\textsuperscript{2} regions. Conversely, the G band, which is normally found between 1500 and 1650 cm\textsuperscript{-1}, is active for all sp\textsuperscript{2} carbon sites, including but not limited to six membered aromatic rings.
Therefore, by comparing the total number of sp\(^2\) sites, with the total number of six
membered rings near edges and defect sites, it is possible to gauge the disorder present in
the sample. This is achieved by comparing the intensities of the D and G peaks. An
experimental relationship known as the Tuinstra and Koenig (TK) equation is noted in the
literature (Equation 24).\(^{118}\)

\[
\frac{I_D}{I_G} = \frac{C(\lambda)}{L_a} 
\]

\text{Equation 31}

where \(I_D\) and \(I_G\) are the intensities of D and G bands respectively, \(C\) is a constant which varies
depending on the wavelength of the laser used, and \(L_a\) is the average size of sp\(^2\) carbon
domains. However, the TK equation is shown to only apply for sp\(^2\) domain sizes larger than
20Å,\(^{117}\) and therefore a separate relationship is suggested in the literature for the domain
sizes under 20Å,

\[
\frac{I_D}{I_G} = C'(\lambda)L_a^2 
\]

\text{Equation 32}

Where \(C'\) is another constant which depends on the wavelength of the laser used. In this
region, the intensity of the D peak is reduced as disorder increases. This is because the 6
membered rings responsible for the D peak are disrupted by the high level of disorder (\(L_a < \)}
The combination of these two equations, with the appropriate constants for C and C’ determined by the wavelength of the laser used, leads to a relationship between \( I_D/I_G \) ratio and the average \( sp^2 \) domain size as shown in Figure 2.3.3. Various other methods of quantifying disorder in graphitic materials have been put forward, including the position of the G and D peaks, and the broadening of the G peak but the standard measure of choice remains as the \( I_D/I_G \) ratio. This may lead to errors in disorder assessments as \( I_D/I_G \) values are quoted without any additional information, leading to ambiguity over which region of the graph is most applicable. A suggested method for determining the correct region of the graph is by examining the extent of peak broadening, as the D and G peaks are shown to increase with disorder. The use of \( I_D/I_G \), while originally observed in all-carbon graphitic systems, has also been shown to apply to GO and rGO samples, with results showing strong agreement with high resolution transmission electron microscopy of GO and rGO.

**FIGURE 2.3.3 (A) THE VARIATION OF \( I_D/I_G \) RATIO COMPARED WITH AVERAGE \( sp^2 \) CLUSTER SIZE (\( L_e \)) USING A RAMAN LASER OF 514nm WAVELENGTH. (B) THE VARIATION OF \( I_D/I_G \) AND G PEAK POSITION WITH RESPECT TO \( sp^3 \) CARBON CONTENT. \( a-G \), \( ta-C \) and \( nc-G \) REPRESENT AMORPHOUS CARBON, TETRAHEDRAL AMORPHOUS CARBON AND NANOCRYSTALINE GRAPHITIC CARBON RESPECTIVELY. (REPRINTED WITH PERMISSION FROM REF 117. COPYRIGHT 1999 AMERICAN PHYSICAL SOCIETY.)**

### 2.3.2 Thermogravimetric Analysis

Thermogravimetric analysis is a technique which involves measuring the weight of material present in a sample as it is heated to a high temperature at a controlled heating rate. As the temperature is increased, volatile products are released as gases, causing a loss in mass. As a technique, it is often used to determine the thermal stability of various materials. In
addition, it is possible to change the external environment that the sample is heated in, as different atmospheric conditions can change the thermal stability of the material being analysed. For example, carbonaceous materials will typically breakdown at a lower temperature in the presence of oxygen, as they decompose to form carbon gases such as carbon dioxide and carbon monoxide. TGA can also be used to determine the extent of inorganic matter in a sample, as inorganic materials, with higher decomposition temperatures, remain present after the organic material has decomposed. This is can be useful for the analysis of carbon materials functionalised with metal nanoparticles for example.

In practice, a TGA sample is loaded into a crucible, which is placed on a weighing stage in a temperature controlled furnace. The temperature and weight is subsequently recorded as the sample is subjected to a heating profile. This heating profile commonly increases the temperature at a constant rate, although more complex heating profiles are sometimes used.

For most carbon nanomaterials, a typical in-air TGA profile will have 2 main mass loss regions. The first occurs between 50 - 150°C and is associated with the loss of solvent molecules, including water, as well as desorption of adsorbed gases from the surface. The second region, associated with thermal decomposition of carbon material through oxidation occurs in a wide range from approximately 500 - 900°C. It is suggested that defect sites such as edges, vacancies and dangling bonds, lead to a decrease in oxidative stability for carbon materials, resulting in the identification of a variety of thermal decomposition temperatures. Typically for GO, a third mass loss region is found at approximately 150 - 190°C which is associated with the initial thermal reduction of GO to rGO. However, TGA coupled with a mass spectrometer has shown that additional water, likely trapped within the GO layers, is lost in this region (Figure 2.3.4).
2.3.3 X-RAY DIFFRACTION

X-ray diffraction (XRD) is an X-ray based technique which looks at the crystallinity of materials. A crystalline material has atoms which are arranged in a regular pattern or lattice, as opposed to an amorphous material which is arranged randomly. This crystallinity results in unique diffraction pattern when X-rays interact with the material. When X-rays hit the nucleus of an atom at a specific angle (θ), the X-ray is reflected outwards by the same angle θ (180° – θ if measured from the original plane). This becomes more important when applied to a crystalline layered structure with a defined distance between the layers (known as the d spacing). In Figure 2.3.5, The X-ray wave hitting top layer traverses path A, while the X-ray wave hitting the layer below separated by distance d from the top layer, traverses as path B. If the layers are separated by distance d then the difference in distance between path A and B is calculated as 2dsinθ using trigonometry as shown. If 2dsinθ is equal to the wavelength of the X-ray used (or the wavelength multiplied by an integer value), constructive interference of the waves occurs, increasing the intensity of return signal at specific angles. This forms the basis of Bragg’s law\textsuperscript{123} (Figure 2.3.5).

\begin{figure}
\centering
\includegraphics[width=\textwidth]{figure2.3.4.png}
\caption{TGA-MS profile for GO where m/z 18, 28, 44 and 64 are water (H\textsubscript{2}O), carbon monoxide (CO), carbon dioxide (CO\textsubscript{2}) and sulphur dioxide (SO\textsubscript{2}) respectively. The sulphur dioxide is theorised to be caused by sulphur based impurities produced in the Hummers method. (Reprinted with permission from REF 57. COPYRIGHT 2012 ELSEVIER) }
\end{figure}
\[ n\lambda = 2d \sin \theta \]

**Figure 2.3.5 Graphical Depiction of Bragg's Law**

Where \( n \) is an integer, \( d \) is the interlayer spacing and \( \theta \) is the angle of incidence for the X-ray of wavelength \( \lambda \). The red arrows represent the difference in distance between path A and path B measuring a total of \( 2dsin\theta \).

Using this relationship, and by scanning across a range of angles with a set X-ray wavelength, it is possible to determine the \( d \) spacing between atoms in the material. An XRD set up utilises a monochromator to restrict the wavelength of X-rays to a single wavelength and a rotation stage, to ensure a suitable range of angles are sampled. Powder XRD utilises the bulk material, and therefore interacts with all possible orientations, allowing for \( d \) spacing’s of the 3D crystal structure to be calculated. Furthermore, the diffraction pattern can be used to determine distance between atoms that regularly repeat in the crystallite structure in any plane. These are given as Miller indices, \(^{124}\) which relate to the planes associated with the unit cell.

A unit cell is defined as the smallest repeating unit that can be used to fully describe a lattice structure (such as a crystallite with a repeating pattern). Graphite typically stacks in an ABAB configuration giving rise to a hexagonal crystal system. The unit cell of a hexagonal crystal system can be described where the lines \( a = b \neq c \) and the angle \( \gamma = 120^\circ \) (Figure 2.3.6). The Miller indices that give rise to peaks in a hexagonal crystal structure are defined as \( h, k, \) and \( l \), which are related to the \( d \) spacing and \( a, b, \) and \( c \) as follows,

\[
\frac{1}{d_{hkl}^2} = \frac{4}{3a^2}(h^2 + hk + k^2) + \frac{l^2}{c^2} \quad \text{Equation 33}
\]
where \( d_{\text{hkl}} \) is the d spacing for the plane defined by the Miller indices values. Using this equation, it is possible to determine the lattice constants from the d spacing and the Miller indices.

From XRD analysis it is also possible to estimate the size of crystallite domains using the Scherrer equation\(^{126}\) which states,

\[
L = \frac{K\lambda}{\beta \cos \theta}
\]

Equation 34

where \( L \) is the crystallite size, \( K \) is a constant known as the shape factor (normally given as 0.9 for \( L_c \) or 1.84 for \( L_a \))\(^{127}\) and \( \beta \) is the peak width at half of the maximum height (known as the full width half maximum or FWHM). By using this equation, and relating it to the peaks which correspond to the in plane Miller indices (i.e. where \( l = 0 \)) it is possible to estimate the average crystallite size, and compare that with the average \( \text{sp}^2 \) size provided by Raman spectroscopy however the errors in estimations between the two techniques can be very high.\(^{128}\)
2.3.4 Ultra violet – visible spectroscopy
Ultra violet – visible (UV-Vis) spectroscopy is an optical absorption technique which utilises the UV and visible wavelengths of the spectrum, from approximately 175 – 800 nm. In a typical UV-Vis set up, a monochromator is used to allow the incident wavelength to be selected and cycled sequentially through the UV and visible light range. This monochromated incident light is then split using mirrors into 2 identical incident beams, one of which is used as a reference beam. The reference placed in the reference beam is dependent on the sample being measured (i.e. for a sample in solution, the pristine solvent is placed in the reference beam in a matching cuvette). The analysis beam interacts with the sample after which both the sample and reference beams are detected separately. A ratio of the intensities ($I_0/I$) is then produced.

Compared to the weaker vibrational transitions found in Infrared spectroscopy, in the UV-visible region light photons have enough energy to cause electronic transitions across the band gap. Typically, these electronic transitions will excite electrons from bonding orbitals in the valance band, (such as the HOMO level) to an orbital in the conduction band (such as the LUMO level). This transition within the sample absorbs the light, allowing a change in light beam intensity to be detected. The types of electronic transitions possible are displayed in Table 2.3-1. The different types of transitions utilise 3 types of orbitals, the $\sigma$ bonding and anti-bonding orbitals which involve end to end orbital overlap, the $\pi$ bonding and anti-bonding orbitals which involve side-on orbital overlap, and finally the non-bonding orbitals which use electrons not involved in bonding (e.g. lone pair electrons).

**Table 2.3-1 Electronic transitions which cause absorption visible in the UV-Vis region.**

<table>
<thead>
<tr>
<th>Transition</th>
<th>Description</th>
<th>Example</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\sigma - \sigma^*$</td>
<td>$\sigma$ bonding to $\sigma$ anti-bonding orbital transition</td>
<td>Methane (122nm)</td>
</tr>
<tr>
<td>$\pi - \pi^*$</td>
<td>$\pi$ bonding – $\pi$ anti-bonding orbital transition</td>
<td>Benzene (254nm)</td>
</tr>
<tr>
<td>$n - \pi^*$</td>
<td>Non-bonding to $\pi$ anti-bonding orbital transition</td>
<td>Acetone (290nm)</td>
</tr>
<tr>
<td>$n - \sigma^*$</td>
<td>Non-bonding to $\sigma$ anti-bonding orbital transition</td>
<td>Methanol (190nm)</td>
</tr>
</tbody>
</table>

The intensity of the light absorbed by a sample can be defined using the Beer-Lambert Law. Absorbance is given as,

$$A = \log_{10} \frac{I_0}{I} = \epsilon l c$$

*Equation 35*
where $I$ and $I_0$ represent the transmitted intensity and the incident intensity respectively, $\varepsilon$ is the molar absorption coefficient, $l$ is the path length and $c$ is the concentration of the analyte. Therefore, for a set path length and known concentrations, it is possible to calculate the absorption coefficient for a substance by setting up a calibration curve. This calibration curve allows for the estimation of unknown concentrations of the substance.

The position of maximum absorption ($\lambda_{\text{max}}$) is highly dependent on the band gap of the material under investigation. For example, it is possible to shift the absorption maxima, by increasing the conjugation length of the analyte material. Conjugation is a term used to describe a chemical structure with alternating single and double bonds, which allow for electron delocalisation through resonance. This increase in delocalisation increases the number of bonding and anti-bonding orbitals, which in turn broadens the size of the conduction and valance bands, which decreases the size of the band gap resulting in a shift of $\lambda_{\text{max}}$. It is therefore possible to estimate the band gap from the UV-Vis data. This is achieved by plotting a Tauc plot, where the energy of light ($h\nu$) is plotted against $(\alpha h\nu)^{1/r}$ and where $r$ is dependent on the type of band gap ($r = 0.5$ for direct band gap, $r = 2$ for indirect band gap). It is suggested that the GO has a band gap ranging from $3.5 - 0.02$ eV with increasing reduction time using hydrazine (Figure 2.3.7).\textsuperscript{129,130} It is also suggested that GO films can be considered as having have a direct optical band gap.\textsuperscript{131} The optical band gap can also be measured using photoluminescence spectroscopy (PL), in which a laser excites electrons to the LUMO level and the band relaxation (such as fluorescence) back to the HOMO level is measured to estimate the band gap.\textsuperscript{132}
2.3.5 Fourier Transform Infrared Spectroscopy

Infrared spectroscopy (IR) is another vibrational measurement technique similar to Raman spectroscopy, which utilises the lower energy wavelengths of the infrared part of the electromagnetic spectrum. These wavelengths, (from approximately 2.5 – 25 μm) have just enough energy to excite molecules into an excited vibrational / rotational state. The presence of specific vibrational / rotational states will depend greatly on the functional groups present, and therefore infrared spectroscopy is an effective tool for discerning the functional groups in organic compounds. The vibrational modes that are considered IR active are determined based on whether a change in dipole moment occurs as it vibrates. This is in contrast to Raman spectroscopy in which modes are active based on changes in polarizability as previously discussed. A schematic energy level diagram comparing IR, Raman, and UV-Vis spectroscopy is provided in Figure 2.3.8.
A typical infrared spectrophotometer has a similar set up to UV-Vis spectrophotometer, with a monochromator cycling the wavelengths to establish a full spectrum. However, in Fourier transform infrared spectroscopy (FTIR) the whole spectrum is scanned simultaneously. This is achieved through the use of an interferometer, utilizing a mathematical process known as a Fourier transformation to discern the absorption at each wavelength of the spectra. This greatly improves the quality of the infrared spectra and also reduces the time taken to acquire data.

Absorption peaks in infrared spectra are commonly compared to known values present in data tables. A set of references tables for IR spectroscopy are included in the appendices (Table 10.1-1). The main vibrational modes associated with oxygen functional groups that are IR active involve bending or stretching of the functional groups. However, the wide range of oxygen functionalities present in GO makes definitive assignment of specific vibrational modes difficult.

2.3.6 IMAGING TECHNIQUES

Imaging techniques allow for the visualisation of an object which would normally be invisible to the human eye. The simplest form of this is the use of magnifying lenses in optical microscopy. However, there is a fundamental limit to the resolution of optical microscopy, which is defined using the following equation,

$$d = \frac{\lambda}{2n \sin \alpha}$$  \hspace{1cm} \textit{Equation 36} \\

where $d$ is the resolution distance, $\lambda$ is the wavelength of the incident light $n$ is the refractive index and $\alpha$ is the semi-aperture angle of lens.\textsuperscript{134} Considering the wavelength of visible light is from 400 – 800 nm, the smallest value of $d$ is approximately 200 nm using conventional lenses and visible light. In order to image with higher resolution, more advanced techniques are required such as scanning electron microscopy (SEM), transmission electron microscopy (TEM) and atomic force microscopy (AFM).

SEM utilises high energy electrons (0.2 – 40KeV) to image objects with higher resolution than standard optical microscopy. In SEM, an electron beam is emitted at low vacuum from an electron gun (normally comprised of a tungsten electrode). This electron beam is
directed and focused by a series of lenses, until it reaches the sample. The interactions of these high energy electrons with the atoms in the sample give rise to various signals, caused by scattering and emission of secondary electrons, which can be recorded with specialised detectors allowing high resolution images to be taken of the surface of a sample. It is however limited to conducting materials, as non-conducting materials are unable replenish the scattered secondary electrons, causing a build-up of electrostatic charge which can distort the image. SEM is also limited to viewing the surface of the material, and therefore cannot give information of the morphology of materials under the surface, or provide information on the surface roughness of the material being imaged.

TEM uses a similar set up to SEM, with an electron beam being focused through a series of lenses until it reaches the surface. However, while SEM detects the scattered electrons that are present, TEM detects the electrons that are transmitted through the sample. This allows for images to be taken which provide information about the material below the surface. However, TEM samples must be very thin to allow the transmission of electrons, unlike SEM samples in which thickness is not important. Moreover, TEM can only analyse very small samples, while SEM is capable of scanning very large samples quickly. Finally, while both SEM and TEM require vacuum conditions, TEM requires a much higher vacuum, which limits the techniques ability to process samples quickly.

In contrast, AFM utilises a scanning probe which can acquire images of a surface at the nanoscale level. A very sharp tip, attached to a cantilever, is tapped progressively across a surface. The movement of the cantilever is monitored using a laser, allowing for the detection of changes in height across the surface. This technique is useful for determining the overall surface roughness of a thin film, or the thickness of a thin film via a scratch method. A scratch method involves gently scratching off an area of the thin film, and measuring the height difference between the thin film surface and the scratch depth. AFM can be run in ambient conditions, however it must be run slowly to ensure the tip is not damaged.

### 2.3.7 X-Ray Computed Tomography

X-ray CT is a commonly used technique in the field of medical imaging. For example, CT scans are used to image the brain to investigate possible tumours or brain injuries. A
series of X-ray images are taken at differing angles, and algorithmically converted to slices. These slices are combined to give a 3D reconstruction of the material being imaged. When X-rays pass through an absorbing material, the X-ray are attenuated either by absorption or scattering. The process of absorption occurs through the photoelectric effect which is demonstrated in Figure 2.3.9. In brief, high energy photons collide with electrons in the inner shell of the target atom, and the energy of the photon is transferred to the electron causing it to be ejected from the atom as a photoelectron. The probability of the photoelectron effect occurring ($\tau$) can be described as the following,

$$\tau \propto \frac{Z^3}{(hv)^3} \quad \text{Equation 37}$$

where $Z$ is the atomic number of the element. Therefore, elements with a higher atomic number will attenuate a higher proportion of X-rays, making it possible to see contrast between elements with different atomic numbers. This contrast is vital in various techniques such as medical X-ray imaging, which uses the contrast between calcium ($Z = 20$) in bone and organic tissue, which is predominately made up carbon, oxygen and hydrogen ($Z = 6, 8$ and $1$ respectively), to image bone structure. An example of a micro-CT reconstruction for a CNT scaffold is shown in Figure 2.3.10.\textsuperscript{139}

\textit{FIGURE 2.3.9 X-RAY ABSORPTION THROUGH THE PHOTOELECTRIC EFFECT, A PHOTON WITH ENERGY (hv) IS ABSORBED AND A PHOTOELECTRON WITH ENERGY (hv – Eb) IS EJECTED FROM THE INNER ELECTRON SHELL. Eb REPRESENTS THE BINDING ENERGY ASSOCIATED WITH THE ELECTRON.}
FIGURE 2.3.10 REPRESENTATIVE 3-D RECONSTRUCTED MICRO-CT IMAGE OF MULTI WALLED CNT SCAFFOLD, AND THE (B) TOP, (C) MIDDLE AND (D) BOTTOM MICROCT SLICE OF THE RECONSTRUCTED 3-D MWCNT SCAFFOLD IMAGE. THE BLUE COLOUR IN THE IMAGES REPRESENTS VOID SPACES. SCALE BARS: (A) 100 μm, (B–D) 300 μm (REPRINTED WITH PERMISSION FROM REF 139 COPYRIGHT 2014 ELSEVIER).

2.4 SUMMARY
In this chapter, a brief introduction to carbon nanomaterials is presented, focusing primarily on sp\(^2\) and sp\(^3\) hybridised atomic orbitals and their presence in different carbon allotropes, such as graphite and diamond. The two dimensional electrical conduction properties of graphite are discussed with respect to the extended delocalisation of π bonding orbitals, which also results in the zero band gap of graphene. After a brief introduction of graphene as a material, a variety of graphene production methods are evaluated, highlighting the limitations of graphene with respect to its use in mass produced practical applications. As a possible alternative, GO and rGO are introduced, displaying favourable solubility properties at the cost of residual oxygen functional groups and sp\(^3\) defects, leading to a decrease in conductivity. Given the solution process-ability of GO, coupled with the ability to functionalise GO/rGO materials, GO presents a platform material suitable to improve a variety of applications. Three such applications are examined in detail: transparent conducting electrodes for use in flexible electronics, charge transport membranes for improved OPV devices, and sorption membranes for environmental remediation. Finally, a selection of spectroscopic and imaging techniques are described which can be used to characterise GO/rGO materials for use as either two dimensional thin films or three dimensional adsorbent sponges.
3 The Synthesis and Characterisation of Graphene Oxide Materials

3.1 Introduction
In this chapter, the methods of synthesising GO based materials used in this thesis are explained. Any other materials synthesised which involve a subsequent reduction step are included in a later section (Chapter 4). Variations on the Hummer’s method are detailed and used to investigate the effect of changes to the traditional processes presented in the literature. These modifications are intended to demonstrate two major points: firstly, that the scaling up of the Hummers’ method does not lead to degradation in material quality, as measured by disorder parameters, and secondly that the Hummers’ method can be tuned to vary the properties of the GO material produced. All GO based materials produced in this thesis are analysed using various spectroscopic techniques, including: Raman spectroscopy (Section 3.3), thermogravimetric analysis (Section 3.4), X-Ray diffraction (Section 3.5), ultra-violet visible spectroscopy (Section 3.6) and Fourier transform infrared spectroscopy (Section 3.7). Imaging and characterisation of deposited GO films using scanning electron microscopy and atomic force microscopy are provided in a later chapter (Section 5.3). The overall aim in this chapter is to determine the best techniques for characterising the GO-based materials produced allowing for the optimisation of properties for use in the application sphere. This chapter also serves to help understand which techniques are complementary to each other, to maximise the ease of characterisation of specific physical properties.

3.2 Synthesis of Graphene Oxide Based Materials
Graphite oxide was prepared from graphite powder via a modified Hummers and Offeman process. Graphite powder (Fisher Chemicals, general purpose grade, G/0900/60) was added to concentrated sulphuric acid under stirring and cooled to 0°C via an ice bath. To this, sodium nitrate (NaNO₃) was added, followed by the careful addition of potassium permanganate (KMnO₄). During this step, the rate of addition was adjusted in order to maintain the temperature below 20°C. After addition, the ice bath was removed and the reaction stirred for 30 minutes in ambient conditions, before the addition of deionised water which prompted a sharp increase in temperature, to ~98°C. After a further 15 minutes, the reaction was terminated through the addition of deionised water and 30%
H$_2$O$_2$ solution. The precipitate produced was separated and washed repeatedly via centrifugation, first with 5% hydrochloric acid and then with deionised water, before being dried under vacuum at 50°C. The quantities of the reactants used are listed in Table 3.2-1.

**TABLE 3.2-1 WEIGHTS OF STARTING REACTANTS AND YIELDS FOR THE GO$_{HMx}$ SERIES**

<table>
<thead>
<tr>
<th>Hummers Method (HMx)</th>
<th>GO$_{HM1}$</th>
<th>GO$_{HM2}$</th>
<th>GO$_{HM3}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite Powder</td>
<td>500 mg</td>
<td>1000 mg</td>
<td>2000 mg</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>11.5 ml</td>
<td>23 ml</td>
<td>46 ml</td>
</tr>
<tr>
<td>Sodium Nitrate</td>
<td>0.25 g</td>
<td>0.5 g</td>
<td>1.0 g</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>1.5 g</td>
<td>3.0 g</td>
<td>6.0 g</td>
</tr>
<tr>
<td>First Water Addition</td>
<td>23 ml</td>
<td>46 ml</td>
<td>92 ml</td>
</tr>
<tr>
<td>Second Water Addition</td>
<td>70 ml</td>
<td>140 ml</td>
<td>280 ml</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>5 ml</td>
<td>10 ml</td>
<td>20 ml</td>
</tr>
<tr>
<td><strong>Final Yield</strong></td>
<td>900 mg</td>
<td>1800 mg</td>
<td>3800 mg</td>
</tr>
</tbody>
</table>

The final yields of 900 mg, 1800 mg and 3800 mg for GO$_{HM1}$, GO$_{HM2}$ and GO$_{HM3}$ respectively, demonstrates a weight increase of approximately 80 - 90% after oxidation. This weight increase is attributed to a combination of oxygen functional groups and some residual water trapped between the layers. As previously discussed in Section 2.1.3, it has been shown that the most prominent oxygen functional groups in GO are alcohol groups (C-OH), carboxylic acids (-COOH) and epoxide (C-O-C) groups. If it is assumed that all the additional weight is caused by these oxygen functional groups, a rough estimation of O:C can be determined. Hypothetically, if all the oxygen functional groups were epoxides, then all the additional weight would be oxygen and the O:C ratio would be 1:1.5 for GO$_{HM1}$ and GO$_{HM2}$, and 1:1.6 for GO$_{HM3}$. Similarly, if all the oxygen functional groups were alcohol groups, there would be a O:H ratio of 1:1, resulting in a slightly higher O:C ratio of 1:1.6 for GO$_{HM1}$ and GO$_{HM2}$ and 1:1.8 for GO$_{HM3}$. However, due to the presence of water trapped between the layers, the weight increase cannot be used as a direct measure of oxygen functionality, but can serve as a rough estimation of oxidation degree. From this initial estimate, it is suggested that the scaling up of the Hummers’ method process has not affected significantly the amount of oxygen functionality present.

To investigate the effect that the amount of KMnO$_4$ oxidiser has on the oxidation of GO, the synthesis method was simplified slightly, and the quantity of KMnO$_4$ used was adjusted (Table 3.2-2). Sodium nitrate was removed from the synthesis method used for the GO$_{HMx}$ series, to limit the number of additional oxidizing agents present. In brief, graphite powder
was added to concentrated sulphuric acid while stirring in a round bottom flask, and specific quantity of KMnO₄ added and stirred until the contents were homogeneous. The round bottom flask was then heated to 50°C for 3 hours, before termination by water and hydrogen peroxide as before. Finally, the precipitate was washed repeatedly via centrifugation, first with 5% hydrochloric acid, then with deionised water, before being dried under vacuum at 50°C. The final yields of 540 mg, 620 mg, 855 mg, 1000 mg, 940 mg and 1100 mg, for GO_MRH11 – GO_MRH16 respectively, shows an increase in weight compared with the starting graphite weight in all cases, as well as an increase in weight increase across the series, indicating an increase in oxidation degree through the series. Using the same O:C estimation technique as previous, the yield estimated minimum O:C ratios of the GO_MRHxx series were worked out and are also provided.

<table>
<thead>
<tr>
<th>Mixed Ratio Hummers (MRH)</th>
<th>GO_MRH10</th>
<th>GO_MRH11</th>
<th>GO_MRH12</th>
<th>GO_MRH13</th>
<th>GO_MRH14</th>
<th>GO_MRH15</th>
<th>GO_MRH16</th>
</tr>
</thead>
<tbody>
<tr>
<td>Graphite : Oxidiser</td>
<td>1:0</td>
<td>1:1</td>
<td>1:2</td>
<td>1:3</td>
<td>1:4</td>
<td>1:5</td>
<td>1:6</td>
</tr>
<tr>
<td>Graphite Powder</td>
<td>500 mg</td>
<td>500 mg</td>
<td>500 mg</td>
<td>500 mg</td>
<td>500 mg</td>
<td>500 mg</td>
<td>500 mg</td>
</tr>
<tr>
<td>Sulphuric Acid</td>
<td>15 mL</td>
<td>15 mL</td>
<td>15 mL</td>
<td>15 mL</td>
<td>15 mL</td>
<td>15 mL</td>
<td>15 mL</td>
</tr>
<tr>
<td>Potassium Permanganate</td>
<td>0 g</td>
<td>0.5 g</td>
<td>1.0 g</td>
<td>1.5 g</td>
<td>2.0 g</td>
<td>2.5 g</td>
<td>3.0 g</td>
</tr>
<tr>
<td>Water</td>
<td>150 mL</td>
<td>150 mL</td>
<td>150 mL</td>
<td>150 mL</td>
<td>150 mL</td>
<td>150 mL</td>
<td>150 mL</td>
</tr>
<tr>
<td>Hydrogen Peroxide</td>
<td>10 mL</td>
<td>10 mL</td>
<td>10 mL</td>
<td>10 mL</td>
<td>10 mL</td>
<td>10 mL</td>
<td>10 mL</td>
</tr>
<tr>
<td>Final Yield</td>
<td>500 mg</td>
<td>540 mg</td>
<td>630 mg</td>
<td>855 mg</td>
<td>1000 mg</td>
<td>940 mg</td>
<td>1100 mg</td>
</tr>
<tr>
<td>Yield Min O:C ratio (Estimate)</td>
<td>1:17,2</td>
<td>1:5,3</td>
<td>1:1,9</td>
<td>1:1,4</td>
<td>1:1,6</td>
<td>1:1,1</td>
<td></td>
</tr>
</tbody>
</table>

3.3 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA RAMAN
All of the GO samples produced as detailed in Section 3.2 were examined using Raman spectroscopy in order to allow for the structural disorder caused by the oxidation process to be examined. For sample preparation, graphite oxide powder was dispersed in water, and sonicated for 10 minutes using a probe sonicator (Cole-Parmer Ultrasonic Processor). To ensure no large clusters of unreacted material remained, the solution was left to settle overnight (approx. 16h) and then the top layer decanted. This solution was then drop casted onto cleaned silicon substrates and measured. The technique of Raman spectroscopy and its uses in graphene based materials is described in detail in Section 2.3.1. All Raman examinations were conducted using a Renishaw 2000 microRaman spectrometer, using a 514 nm laser excitation wavelength. Prior to use, the Raman microscope was calibrated.
against a silicon standard. For all GO samples presented, a total of 10 - 12 scans were accumulated, across 3 different locations in the sample, to reduce the significance of errors and anomalies. As a reference, the Raman spectrum for the starting graphite is shown in Figure 3.3.1 and is compared with a pristine sample of highly ordered pyrolytic graphite (HOPG). The major peaks seen in both the powdered starting graphite and the HOPG are present at 1575 cm$^{-1}$ and 2710 cm$^{-1}$. These are the G peak and the 2D peaks respectively. The only visible difference is a small peak at 1344 cm$^{-1}$ (highlighted in grey), which is the D peak. The presence of the D peak in the starting graphite is explained by the presence of defects at the graphite edges which will give rise to the D peak.

The Raman spectrum for GO shares these prominent features but also differs in a few ways. One of the major ways the GO Raman spectrum differs from the graphite spectrum is based on the intensity of the photoluminescence background. This background must be subtracted before peaks can be analysed and compared. After background subtraction, the G, D and 2D peaks become visible, as well as the addition of peaks present at approx. 2950 cm$^{-1}$ and 3150 cm$^{-1}$, which are commonly labelled as the D+G and 2D’ overtones respectively. These peaks can all be seen in Figure 3.3.2 which shows a typical GO Raman spectra. By applying a Lorentzian peak fitting process it is possible to map the GO Raman spectrum
using these five peaks. This allows for the quantitative analysis of properties such as the peak intensity, area and width via the FWHM.

**FIGURE 3.3.2 LORENTZIAN PEAK FITTING OF A GO RAMAN SPECTRA. THE PEAKS ARE CENTERED AT THE POINT OF HIGHEST INTENSITY FOR EACH PEAK APPROXIMATELY 1355, 1590, 2710, 2950 AND 3150 cm\(^{-1}\) IN THIS CASE CORRESPONDING TO THE D, G 2D, D+G AND 2D' BANDS RESPECTIVELY.**

Figure 3.3.3 shows the Raman spectra for the GO\(_{H_{Mx}}\) series. As expected all five peaks seen with GO are present with very little variation when compared with a sample spectra for GO (Figure 3.3.2). The D and G peaks are both present throughout the series. The analysis of the peak position, widths (measured at the FWHM) and D/G ratios for both area and intensity are included in Table 3.3-1. Considering the standard deviations associated with the measurements, and the instrumental resolution of Raman measurements (2 cm\(^{-1}\)), the peak positions, and peak widths can be considered equivalent throughout the GO\(_{H_{Mx}}\) series. The D and G peak positions for the GO\(_{H_{Mx}}\) series are 1356 ± 3 cm\(^{-1}\) and 1590 ± 3 cm\(^{-1}\) respectively, with D and G peak widths (FWHM\(_D\) and FWHM\(_G\)) of 118 ± 6 cm\(^{-1}\) and 72 ± 5 cm\(^{-1}\) respectively. Comparing these values with values ascertained for the starting graphite material, it is clear that both the D and G peaks for the GO\(_{H_{Mx}}\) series have shifted to higher values after oxidation. There is also an increase in both peak widths from the powder graphite starting values of 47 cm\(^{-1}\) and 26 cm\(^{-1}\) for the FWHM\(_D\) and FWHM\(_G\) respectively. Both the shifting of the D and G peaks and the broadening of the peaks indicate an increase in disorder compared to the starting graphite material, which will be discussed further later in the section.
FIGURE 3.3.3 RAMAN SPECTRA FOR THE GO$_{HM}$ SERIES WITH PEAKS HIGHLIGHTED AT APPROXIMATELY 1355, 1590, 2705, 2935 AND 3165 cm$^{-1}$ WHICH HIGHLIGHT THE D, G, 2D, D$+$G AND 2D$'$ BANDS RESPECTIVELY.

TABLE 3.3-1 D/G PEAK ANALYSIS FOR THE GO$_{HM}$ SERIES

<table>
<thead>
<tr>
<th></th>
<th>Peak Position (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>D/G Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>D Peak</td>
<td>G Peak</td>
</tr>
<tr>
<td>GO$_{HM1}$</td>
<td>1354 ± 1</td>
<td>1588 ± 2</td>
<td>119 ± 2</td>
</tr>
<tr>
<td>GO$_{HM2}$</td>
<td>1356 ± 3</td>
<td>1590 ± 2</td>
<td>118 ± 5</td>
</tr>
<tr>
<td>GO$_{HM3}$</td>
<td>1356 ± 2</td>
<td>1590 ± 3</td>
<td>117 ± 1</td>
</tr>
</tbody>
</table>

The $I_D/I_G$ ratio of 0.79 ± 0.06 for the GO$_{HM}$ series also shows an increase when compared with the $I_D/I_G$ ratio of the starting material powdered graphite, which has an $I_D/I_G$ ratio of 0.134. Utilising the TK equation and related equations presented in Section 2.3.1, it is possible to estimate the average sp$^2$ carbon domain size. Using values for C and C$'$ suggested in literature for a Raman laser wavelength of 514.5 nm (C = 44Å, C$'$ = 0.0055Å)$^{117}$, the $I_D/I_G$ ratio vs average sp$^2$ cluster size ($L_a$) was plotted as shown in Figure 3.3.4. For an $I_D/I_G$ ratio of 0.79, the equation for Region 1 ($I_D/I_G = C'(\lambda)L_a^2$) as proposed by Ferrari et al.$^{117}$ suggests an average sp$^2$ cluster size of 1.20 nm, while the TK equation for Region 2 ($I_D/I_G = C(\lambda)/L_a$) returns an average sp$^2$ cluster size of 5.56 nm. Both estimates suggest a substantial breakdown of the starting sp$^2$ graphite lattice. In literature, Raman G peak broadening has
been shown to be influenced by stress applied to a graphitic system and the size of sp\(^2\) domains.\(^{119}\) To determine whether the GO material should be classified as Region 1 or Region 2, the FWHM\(_G\) and FWHM\(_D\) values are compared with values presented in the literature for Ar-bombarded graphene.\(^{120}\) It is seen that FWHM\(_G\) and FWHM\(_D\) values for Region 2 are typically below 40 cm\(^{-1}\) as a result of having an average sp\(^2\) cluster size of more than 2 nm, with Region 1 taking values above 40 cm\(^{-1}\) as a result of average sp\(^2\) cluster sizes of less than 2 nm, as illustrated in Figure 3.3.4. This leads to the conclusion that the GO\(_{HMX}\) series resides in the more amorphous Region 1, which is in agreement with high resolution TEM results presented by Erickson \textit{et al.}, which suggest the presence of small sp\(^2\) clusters, approximately 1 nm in diameter surrounded by large oxygen rich regions present in GO.\(^{53}\) It is proposed that these oxygen rich regions present in GO result in the low C:O ratios (ca. 2:1) observed by Chua \textit{et al.},\(^{56}\) as well as an increase of stress on the sp\(^2\) carbon clusters, leading to broadening of the D and G peaks.

\[ \frac{I_D}{I_G} \text{ VS THE AVERAGE sp}^2 \text{ CLUSTER SIZE (L} _a \text{) PLOTTED USING EQUATIONS ESTABLISHED IN LITERATURE WHERE C AND C' EQUAL 44Å AND 0.0055Å RESPECTIVELY.}^{127}\text{ THE BLUE LINE REPRESENTS THE I_D/I_G RATIO FOR THE GO}_{HMX}\text{ SERIES.} \]

The Raman spectra for the GO\(_{MRHxx}\) series (Figure 3.3.5), increases in peak intensity with increasing addition of oxidiser (KMnO\(_4\)). This trend is also seen in the intensity of the background which is also shown. The increased background response (Figure 3.3.5 Part B) is
caused by fluorescence in amorphous carbon materials.\textsuperscript{117} This provides evidence that regions of amorphous carbon are formed in the oxidation of graphite to graphite oxide, and shows an increasing trend of amorphous carbon content in the GO_{MRHxx} series which relates to an increase in disorder. Unfortunately, the background intensities can only be used as a rough estimate for oxidation degree, due to a number of factors, including intensity fluctuations in the laser and variations in sample thickness. For example, the relative standard deviation for the sum of the background intensities for repeats of the GO_{MRH12} spectra has a value of 61.5\%. Therefore, it is common to normalise peaks to another specific peak or the total intensity of the graphs. The peak ratios, positions, and widths for the D and G peaks are presented in Table 3.3-2.

![Figure 3.3.5](image.png)

**Figure 3.3.5** (A) Stacked background subtracted Raman spectra for the GO_{MRHxx} series, (B) the average background taken at 2250 cm\(^{-1}\) plotted for the GO_{MRHxx} series on a log_{10} scale.

**Table 3.3-2** D/G peak analysis for the GO_{MRHxx} series.

<table>
<thead>
<tr>
<th></th>
<th>Peak Position (cm(^{-1}))</th>
<th>FWHM (cm(^{-1}))</th>
<th>D/G Ratio</th>
<th>Area</th>
<th>Intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D Peak</td>
<td>G Peak</td>
<td>D Peak</td>
<td>G Peak</td>
<td></td>
</tr>
<tr>
<td>GO_{MRH11}</td>
<td>1349 ± 1</td>
<td>1590 ± 1</td>
<td>89 ± 2</td>
<td>63 ± 1</td>
<td>1.31 ± 0.01</td>
</tr>
<tr>
<td>GO_{MRH12}</td>
<td>1354 ± 1</td>
<td>1596 ± 1</td>
<td>99 ± 1</td>
<td>60 ± 1</td>
<td>1.39 ± 0.01</td>
</tr>
<tr>
<td>GO_{MRH13}</td>
<td>1357 ± 2</td>
<td>1594 ± 1</td>
<td>115 ± 4</td>
<td>66 ± 1</td>
<td>1.37 ± 0.01</td>
</tr>
<tr>
<td>GO_{MRH14}</td>
<td>1358 ± 3</td>
<td>1593 ± 1</td>
<td>120 ± 5</td>
<td>73 ± 8</td>
<td>1.34 ± 0.09</td>
</tr>
<tr>
<td>GO_{MRH15}</td>
<td>1357 ± 1</td>
<td>1593 ± 1</td>
<td>122 ± 6</td>
<td>73 ± 4</td>
<td>1.34 ± 0.01</td>
</tr>
<tr>
<td>GO_{MRH16}</td>
<td>1359 ± 1</td>
<td>1591 ± 2</td>
<td>128 ± 13</td>
<td>80 ± 11</td>
<td>1.32 ± 0.08</td>
</tr>
</tbody>
</table>
All of the GO_{MRHxx} series show the 5 characteristic peaks expected for GO samples. The presence of a significant D peak in GO_{MRH11} shows a significant degree of change from the starting graphite material. The I_D/I_G for GO_{MRH11} of 0.92 ± 0.03 is higher than the rest of the series. The rest of the series shows an I_D/I_G ratio closer to 0.79 similar to that of the GO_{HMx} series. The widths of the D and G peaks (> 40 cm\(^{-1}\)) suggest that the Region 1 relationship \(I_D/I_G = C'(\lambda) L_a^2\), as proposed by Ferrari et al., applies. Using the equation for Region 1 (depicted in Figure 3.3.4), this suggests an average sp\(^2\) cluster size of approximately 1.29 nm for GO_{MRH11} and 1.20 nm for the rest of the series. This is a very small change considering the difference in weight added as shown by final product yields. This is because the average size of sp\(^2\) clusters is not necessarily proportional to the total disorder in the sample especially at large defect concentrations. Therefore, other potential figures of merit were taken from the Raman data and plotted in Figure 3.3.6 to investigate the disorder content.

For comparison, GO_{MRH10} was added to the series, which involves the addition of no KMnO\(_4\) in the oxidation process. This GO_{MRH10} derivative shows a similar Raman spectrum to powdered graphite as shown previously in Figure 3.3.1.

**FIGURE 3.3.6 POSSIBLE FIGURES OF MERIT DERIVED FROM PARAMETERS OF THE D AND G PEAKS MEASURED BY RAMAN SPECTROSCOPY FOR THE GO_{MRHxx} SERIES**
Figure 3.3.6 shows a number of useful insights about the Raman response of the GO\text{MRHxx} series. The widths of the peaks, as measured by the FWHM also show an increase throughout the series progression. The broadening of both the D and G bands and can be explained in relation to disorder. The broadening of the G band can also be explained by the activation of a defect induced D’ band (1615 cm\(^{-1}\)) in the same region as the G band.\(^{142,143}\) This band is caused by the presence of sp\(^2\) chains rather than aromatic rings. This can be used to explain why the peak position of the G band shows a shift from 1576 cm\(^{-1}\) to approximately 1596 cm\(^{-1}\) between GO\text{MRH10} and GO\text{MRH12} as starting disorder breaks down aromatic sp\(^2\) regions, converting them into sp\(^2\) chains. The progressive shift from 1596 cm\(^{-1}\) to approximately 1591 cm\(^{-1}\) throughout the rest of the series suggests that further oxidation preferentially targets the sp\(^2\) chains over the aromatic sp\(^2\) rings, causing the shift to reverse. This explains why pristine sp\(^2\) clusters can be found in GO samples using high resolution TEM as seen in literature.\(^53\)

The broadening of the D peak is argued to be caused by an overlap of the D band for graphitic materials and new modes caused by sp\(^3\) carbon atoms.\(^{144}\) Alternatively, peak broadening is seen to be caused by stress on sp\(^2\) clusters. It is proposed that increases in disorder content will increase stress on the sp\(^2\) clusters, due to the non-linear nature of sp\(^3\) bonded carbon atoms. It is suggested in literature that the peak broadening is affected by the distribution of sp\(^2\) cluster sizes with a wider range of sp\(^2\) cluster sizes resulting in wider D peak.\(^{117}\) It is reasonable to assume that by increasing the sp\(^3\) carbon content surrounding a sp\(^2\) cluster, the stress exerted on the remaining sp\(^2\) cluster increases. Therefore, the broadening of the D and G peaks are a credible measure of the sp\(^3\) carbon content, and subsequently the disorder of the GO material.

Finally, the position of the D peak is seen to increase 1349 ± 1 cm\(^{-1}\) (GO\text{MRH11}) to 1359 ± 1 cm\(^{-1}\) (GO\text{MRH16}) with increasing oxidation. It is possible that this shift is related to an increase in disorder through the appearance of a disorder based peaks at approximately 1450 cm\(^{-1}\), designated the D” band, as seen in literature.\(^{142}\) The physical origin of this peak is not fully understood, possibly the result of semi-circle ring stretches as seen in benzene.\(^{119}\) The presence of this band could also explain why the width of the D peak grows by a greater extent than that of the G peak. It is also demonstrated that the position of the D peak is
influenced by the application of external stress, which could also lead to a similar response as the peak broadening.  

The positions and widths of the D and G peaks can be compared with the maximum quantity of oxygen functionality, (calculated subtracting the starting graphite mass from the dried product yield) and the minimum O:C ratio (calculated in Section 3.2) (Figure 3.3.7). As previously discussed in Section 3.2, these measures can only be used as rough estimations for the degree of oxidation present in the GO samples, due to the presence of water trapped between the layers. Using these rough estimations, it can be seen that the D and G peaks broaden with increasing oxygen content, as a result of the structural disorder caused by the oxidation process.

![Diagram showing the comparison of D and G peak positions and widths with maximum oxygen functionality and minimum O:C ratio](image)

**Figure 3.3.7** The (left) G and (right) D peak widths and positions plotted as a function of (top) the maximum possible oxygen functionality (Max Oxygen Funct.) and (bottom) the minimum O:C ratio based on product yield calculations. It is possible that water trapped between the layers will shift these values as shown in gray.

### 3.4 Characterisation of Graphene Oxide Materials via TGA

In order to examine the thermal stability of the GO materials produced, thermogravimetric analysis (TGA) was performed on various GO samples. TGA as a technique is described in
detail in Section 2.3.2. TGA was undertaken using a TA Instruments Q500 in air (balance gas, nitrogen: 40 cm$^3$ min$^{-1}$, sample gas, air: 60 cm$^3$ min$^{-1}$). Dried GO Powder was placed on a platinum crucible and heated at a heating rate of 10 K.min$^{-1}$ from room temperature to 900°C. TGA profiles for the GO$_{HMx}$ series are presented in Figure 3.4.1. By plotting the derivative of the weight of the sample throughout the analysis, it is possible to see the mass loss steps present in the sample. For the GO$_{HMx}$ series, there are three significant mass loss steps. The first mass loss step occurs between 50–100°C for all samples associated with the loss of water molecules adsorbed on the surface from the atmosphere. The second region of mass loss occurs between 100–250°C, and is shown as a series of small peaks in the derivative of the GO$_{HMx}$ series. In this region, there are typically 2–3 mass loss steps. All 3 of the GO$_{HMx}$ have 3 definable mass loss steps, which start at 100°C, 150°C and 200°C, and peak at 130°C, 175°C and 235°C respectively. This second mass loss region, between 100–300°C, is theorised to be a combination of trapped water lost from in between the GO layers as rapid expansion occurs, and the pyrolysis of some oxygen functionality, causing thermal reduction of GO.

The last major mass loss step is present between 500–600°C, which corresponds to decomposition of GO in air. This is confirmed in Figure 3.4.2 which shows the effect of atmospheric air on the TGA profile. The mass loss steps from 50–300°C remain unchanged.
by the introduction of a nitrogen atmosphere to the TGA measurement confirming the loss of adsorbed species and oxygen functionality regardless of atmosphere. However, the final mass loss step at 450 – 600°C is not present when the test is conducted in a nitrogen atmosphere. It can therefore be concluded that this mass loss step at 500 – 600°C corresponds to an interaction between the GO material and atmospheric air, to produce carbon oxidation productions (CO and CO₂).

**FIGURE 3.4.2 TGA COMPARISON PLOT OF GO<sub>HMx</sub> UNDER DIFFERENT ATMOSPHERIC CONDITIONS. THE FIRST DERIVATIVE OF THE WEIGHT IS GIVEN AS A DOTTED LINE.**

The TGA analysis for the GO<sub>M</sub>RH<sub>x</sub> series is presented in Figure 3.4.3. All spectra in the series show the same distinct regions as the GO<sub>H</sub>M<sub>x</sub> series, with 3 separate mass loss regions occurring between 50 – 100°C, 100 – 300°C and > 450°C respectively. The first region between 50 – 100°C associated with surface water is similar to the GO<sub>H</sub>M<sub>x</sub> series for GO<sub>M</sub>RH<sub>13</sub> - GO<sub>M</sub>RH<sub>16</sub>. GO<sub>M</sub>RH<sub>11</sub> shows significantly less loss in this region indicating that the quantity of surface water is greatly reduced. Therefore, this region gives a strong indication of the interaction potential with -OH of the material, showing that hydrophobicity decreases as oxidation increases. In hydrophilic samples, this region will also be largely affected by the surface area of the sample as more surface area is available for water to adsorb onto. The second mass loss region, between 100 – 300°C, as previously discussed indicates the amount of trapped water, and the quantity of oxygen functionality that can be removed at low temperatures in a thermal reduction process. Finally, the mass loss region after 450°C shows a decrease in thermal decomposition temperature for samples later in the series. This
is significant as it can be used as an indication of the extent of disorder for the materials, considering that pristine graphene/graphite shows a higher thermal decomposition temperature in air (700 - 800°C). Selective oxidation of carbon species based on disorder is seen in CNTs, with more crystalline samples decomposing at higher temperatures in air. It can be concluded that the increase in oxidation also increases the degree of disorder compared to the pristine graphite starting material as seen in Raman spectroscopy. This is expected as the sp² carbon framework is disrupted with the addition of oxygen bonded to sp³ carbon atoms. Comparisons of the thermal decomposition temperature in air with the characteristics determined through Raman spectroscopy (Section 3.3) are shown in Figure 3.4.4.

**FIGURE 3.4.3 TGA PLOTS FOR THE GO_MRHX SERIES. THE FIRST DERIVATIVE OF THE WEIGHT IS GIVEN AS A DASHED LINE.**
FIGURE 3.4.4 DISORDER TRENDS MEASURED USING RAMAN SPECTROSCOPY PLOTTED AGAINST THE THERMAL DECOMPOSITION TEMPERATURE IN AIR MEASURED USING TGA. THE G PEAK POSITION, WHICH IS INFLUENCED BY THE POSITION OF THE D' PEAK AT 1615 cm⁻¹ CAUSED BY sp² CHAINS IS SHOWN IN RED. GRAPHITE, GO_MR11 AND GO_MR16 ARE LABELLED FOR CLARITY.

By comparing the disorder trends measured using Raman spectroscopy with the thermal decomposition temperature in air, as measured using TGA, trends similar to Section 3.3 can be seen. As the thermal decomposition temperature decreases from 662°C for GO_MR11 to 476°C for GO_MR16, the widths of both the D and G peaks broaden, and the position of the D peak shifts from 1348 cm⁻¹ for GO_MR11 towards 1360 cm⁻¹ for GO_MR16. Additionally, the G peak shows an increase to 1595 cm⁻¹ followed by a decrease to 1591 cm⁻¹ with decreasing thermal decomposition temperature. This trend is similar to the G peak position trend observed when comparing the G peak position with the total product yield, as well as estimates of the maximum oxygen functionality. Therefore, it can be concluded that the thermal decomposition temperature in air can be used to estimate the structural disorder present in GO based materials.
Further examination of the 100 – 300°C region can also give an insight into the degree of oxidation for the material. A detailed breakdown of the mass loss steps in this region is included in Table 3.4-1. To exclude water present on the surface of the samples from the measurement, values were taken from 100°C, up to 350°C where all mass loss at 300°C has finished. In the GO\textsubscript{MRHxx} series, this region is divided into two mass loss steps, before and after approximately 180°C. The overall trend shows that, by increasing the amount of KMnO\textsubscript{4}, the mass loss in this region is increased in the first half of the series, as the second half of the series seems to plateau. Step one (up to approx. 180°C) is caused by the loss of water trapped in-between the layers, as well as the removal of weakly bound oxygen groups on the surface of the GO sheets. This loss of water causes a contraction of the interlayer distance as measurable by XRD. (Section 3.5) Step 2 is caused by the removal of more strongly bound oxygen functionality. In conclusion, examining the 100 – 350°C region can only be used as a rough estimate of the degree of oxidation content, without additional techniques such as mass spectrometry, to accurately determine the content of water trapped between the layers. By comparison, the thermal decomposition temperature in air can be used to corroborate disorder trends suggested by Raman spectroscopy and therefore can be used to estimate disorder present in GO/rGO samples.

**TABLE 3.4-1 TGA MASS LOSS PERCENTAGES FROM BETWEEN 100°C TO 350°C FOR THE GO\textsubscript{MRHxx} SERIES.**

<table>
<thead>
<tr>
<th>Mass loss region*</th>
<th>GO\textsubscript{MRH11}</th>
<th>GO\textsubscript{MRH12}</th>
<th>GO\textsubscript{MRH13}</th>
<th>GO\textsubscript{MRH14}</th>
<th>GO\textsubscript{MRH15}</th>
<th>GO\textsubscript{MRH16}</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mass lost (100 - 350°C)</td>
<td>10.7%</td>
<td>30.2%</td>
<td>48.5%</td>
<td>54.9%</td>
<td>58.6%</td>
<td>52.6%</td>
</tr>
<tr>
<td>Step 1 (100 – ca. 180°C)</td>
<td>3.3%</td>
<td>7.6%</td>
<td>21.5%</td>
<td>31.9%</td>
<td>29.0%</td>
<td>34.3%</td>
</tr>
<tr>
<td>Step 2 (ca. 180 – 350°C)</td>
<td>7.6%</td>
<td>24.4%</td>
<td>34.3%</td>
<td>33.8%</td>
<td>41.7%</td>
<td>27.8%</td>
</tr>
</tbody>
</table>

*100% set to equal the remaining mass at the step starting temperature

**3.5 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA XRD**

To measure the interlayer distances of GO samples, to determine the effects of increasing oxidation on the structure of the GO samples, X-Ray diffraction (XRD) was used as previously described in Section 2.3.3. The Powder X-Ray diffractometer used for XRD analysis was a Panalytical X’Pert Pro, with a Copper X-ray tube and an incident beam graphite monochromator, with Cu K(α) radiation operating at 45 kV and 40 mA. Dried GO powders were synthesised as detailed in Section 3.2 before being finely ground and used in sample preparation. All scans were run for 15 hours, from 3.5 – 90° 2θ, with a resolution of 0.02° 2θ.
The XRD pattern of the starting graphite material used is shown in Figure 3.5.1 with details of the peaks present are given in Table 3.5-1. The major peak present is found at 26.5° which corresponds to the 002 peak for graphite. The 002 lattice plane runs parallel to the graphite layers and therefore measures the distance between the layers, also known as the interlayer distance. The d-spacing for this peak is calculated from the Bragg equation,\textsuperscript{123} to give an interlayer distance of 3.36 Å. Other important peaks include a peak at 42.3° and 44.5° which correspond to the 100 and 101 planes respectively. This first 100 plane is important as it can be used to calculate the distance between carbon atoms C\textsubscript{1} and C\textsubscript{3}, which also corresponds to the a and b distances for the graphite unit cell. Since graphite follows a hexagonal lattice structure where the lattice constants a = b ≠ c, the 100 and 002 are all that is required to work out the dimensions of the graphite unit cell using Equation 33 presented in Section 2.3.3. The graphite unit cell includes 2 layers of graphene stacked in an AB configuration, where the lattice constants are a and b = 2.46 Å and c = 6.72 Å. Using the distance between C\textsubscript{1} and C\textsubscript{3} it is possible to work out the C\textsubscript{1} to C\textsubscript{2} distance. The calculated distance for this is 1.42 Å, which corresponds with values typically reported in literature.\textsuperscript{118}
TABLE 3.5-1 XRD PEAK ASSIGNMENTS FOR THE GRAPHITE STARTING MATERIAL

<table>
<thead>
<tr>
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</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>002</td>
<td>26.51</td>
<td>3.36</td>
<td>291570</td>
<td>134822</td>
</tr>
<tr>
<td>2</td>
<td>100 &amp; 010</td>
<td>42.33</td>
<td>2.13</td>
<td>2127</td>
<td>694</td>
</tr>
<tr>
<td>3</td>
<td>101 &amp; 011</td>
<td>44.48</td>
<td>2.04</td>
<td>3043</td>
<td>1324</td>
</tr>
<tr>
<td>4</td>
<td>004</td>
<td>54.43</td>
<td>1.68</td>
<td>19753</td>
<td>2686</td>
</tr>
<tr>
<td>5</td>
<td>110</td>
<td>77.41</td>
<td>1.23</td>
<td>3976</td>
<td>865</td>
</tr>
<tr>
<td>6</td>
<td>112</td>
<td>83.52</td>
<td>1.16</td>
<td>2064</td>
<td>1123</td>
</tr>
<tr>
<td>7</td>
<td>006</td>
<td>86.87</td>
<td>1.12</td>
<td>2649</td>
<td>1153</td>
</tr>
</tbody>
</table>

The XRD plots for the GO_{HMx} series are shown in Figure 3.5.2, with the major peaks assigned in Table 3.5-2. Comparing these results with the spectrum of the graphite starting material from Figure 3.5.1, both the intra-layer peaks are still present at 42.3° and 77.4° which suggests that most of the hexagonal structure of the graphitic material is maintained within the layers itself. However, the absence of peak at 26.5° suggests that the interlayer distance has changed. This is further supported by the absence of peaks with Miller index l value above 0; i.e. the (101), (004), (112) and (006) peaks, which are present in graphite. These planes are affected by changes to the c parameter of the unit cell and therefore are affected by the interlayer distance, leading to a disappearance in the peak. This is expected as the oxidation process introduces oxygen functionality in between the layers, enlarging the interlayer distance, but also disrupting long range order in the lattice. The new peak at 10.5° is therefore the (002) peak for the GO_{HMx}. This corresponds to an interlayer distance of 8.4 - 8.7Å. This increase in the interlayer distance subsequently increases the height of the unit cell, which greatly enlarges the d spacing of planes with a Miller index l value above 0. This explains why a small curve is observed in the 25 - 40° region of the GO_{HMx} series as the more amorphous stacking of GO sheets gives a wide variety of d spacings, without any significant long range order. Overall, there is very little variation between the samples in the GO_{HMx} series.
FIGURE 3.5.2 XRD PATTERNS FOR THE $\text{GO}_{\text{HMx}}$ SERIES SHOWING NO CHANGE TO THE GO MATERIAL WITH INCREASING BATCH SIZES. PEAK ASSIGNMENTS ARE LABELLED ON THE RESPECTIVE PEAKS FOR $\text{GO}_{\text{HM1}}$

TABLE 3.5-2 XRD PEAK ASSIGNMENTS FOR THE $\text{GO}_{\text{HMx}}$ SERIES

<table>
<thead>
<tr>
<th></th>
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<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{GO}_{\text{HM1}}$</td>
<td>1</td>
<td>002 GO</td>
<td>10.42</td>
<td>8.49</td>
<td>5348</td>
<td>13964</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>004 GO</td>
<td>19.98</td>
<td>4.44</td>
<td>330</td>
<td>287</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>002 Graphite</td>
<td>26.54</td>
<td>3.36</td>
<td>126</td>
<td>274</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>100 &amp; 010</td>
<td>42.42</td>
<td>2.13</td>
<td>6945</td>
<td>6045</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>110</td>
<td>77.25</td>
<td>1.23</td>
<td>1518</td>
<td>1982</td>
</tr>
<tr>
<td>$\text{GO}_{\text{HM2}}$</td>
<td>1</td>
<td>002 GO</td>
<td>10.51</td>
<td>8.41</td>
<td>8579</td>
<td>16802</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>004 GO</td>
<td>20.39</td>
<td>4.35</td>
<td>707</td>
<td>1691</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>002 Graphite</td>
<td>26.64</td>
<td>3.34</td>
<td>255</td>
<td>332</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>100 &amp; 010</td>
<td>42.38</td>
<td>2.13</td>
<td>7230</td>
<td>6293</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>110</td>
<td>77.32</td>
<td>1.23</td>
<td>1532</td>
<td>2000</td>
</tr>
<tr>
<td>$\text{GO}_{\text{HM3}}$</td>
<td>1</td>
<td>002 GO</td>
<td>10.15</td>
<td>8.70</td>
<td>8506</td>
<td>12957</td>
</tr>
<tr>
<td></td>
<td>2</td>
<td>004 GO</td>
<td>20.80</td>
<td>4.27</td>
<td>393</td>
<td>342</td>
</tr>
<tr>
<td></td>
<td>3</td>
<td>006 GO</td>
<td>30.38</td>
<td>2.94</td>
<td>155</td>
<td>471</td>
</tr>
<tr>
<td></td>
<td>4</td>
<td>100 &amp; 010</td>
<td>42.43</td>
<td>2.13</td>
<td>6331</td>
<td>5510</td>
</tr>
<tr>
<td></td>
<td>5</td>
<td>110</td>
<td>77.38</td>
<td>1.23</td>
<td>1423</td>
<td>1548</td>
</tr>
</tbody>
</table>

An overview of the XRD plots for the $\text{GO}_{\text{MRHxx}}$ series are shown in Figure 3.5.3. The significant changes occur between 5 - 30° (highlighted in blue) and 40 - 50° (highlighted in
There is also a decrease of the peak at $77 - 78^\circ$ which is highlighted in green. The significant change in the 5 - 30° region is the shifting of the 002 peak from 26.5° to 9.4° as the series progresses. As seen in Figure 3.5.1, the 002 peak for graphite occurs at 26.5° which corresponds to a d spacing of 3.35 Å. This peak is present as the first major peak in both the $\text{GO}_{\text{MRH11}}$ and $\text{GO}_{\text{MRH12}}$ samples. The interlayer distance for these 2 samples therefore remains similar to graphite as the degree of oxidation is insufficient to separate the layers enough to allow for the breakdown of Van der Waal interactions between the sheets. This means that water is unlikely to be trapped between the layers in these samples. This is consistent with TGA results in Section 3.4 which show significantly lower mass losses between 100 - 180°C region in which the trapped water is removed.

**FIGURE 3.5.3** XRD PATTERNS FOR THE $\text{GO}_{\text{MRHXX}}$ SERIES THE BLUE, RED AND GREEN BOXES HIGHLIGHT THE CHANGES THAT OCCUR IN THE 002, 101 AND 110 IN TABLE 3.5-2 RESPECTIVELY.

From $\text{GO}_{\text{MRH13}}$ onwards, the 002 peak shifts to approximately 9-10°, similar to the $\text{GO}_{\text{HMx}}$ series (as seen in Figure 3.5.2). This transition of the 002 peak is shown in Figure 3.5.4. It should be noted that the peak transition is not a continuous transition, which would suggest a gradual increase in interlayer distance with increased oxygen functionality. Instead, two
discrete stages are seen, a graphite like compact stage with an interlayer distance of ca. 3.35 Å, and a GO like stage, with a much larger interlayer distance of 8-10 Å. Figure 3.5.4 also shows the change in the 40-50° region, where in GO_{MRH11} both the 100 and 101 peaks seen in graphite are present at 42.6° and 44.4° respectively. As the series progresses, the 101 peak disappears from the region, while the 100 remains in the same place. This is further evidence that the interlayer distance is changing as the oxygen functionality is increased from the very graphite like GO_{MRH11}. In summary, the increase in oxygen functionality caused by increased KMnO\textsubscript{4} addition causes the layers of graphite to separate from 3.35 Å to 8-10 Å. This will allow water to permeate between the layers aiding exfoliation, which may be influential for adsorption applications as explored in Chapter 7.

By using the Scherrer equation, it is possible to estimate the average crystallite domain size \(L_a\) using the FWHM of certain peaks. Peaks with a Miller index \(l\) value of 0 can be used, (such as 100 or 110) as the \(d\) spacing is determined solely by the ‘\(a\)’ parameter of the unit cell. Similarly, peaks where the Miller index \(h\) and \(k\) values are 0 (such as the 002 plane) can

---

**FIGURE 3.5.4 PLOTS SHOWING THE 5-30° (TOP LEFT) AND THE 40-50° (TOP RIGHT) REGIONS OF THE GO_{MRHXX} SERIES. THESE HIGHLIGHT THE CHANGE IN THE 002 AND 101 PEAKS RESPECTIVELY. THE BOTTOM PLOT STACKS THE XRD PATTERNS FOR THE GO_{MRHXX} SERIES.**
be used to calculate the thickness of the crystal ($L_a$). By taking the FWHM for the 100 and 110 plane it is possible to estimate the average crystallite domain size on the two dimensional graphene plane and compare it with the average sp$^2$ cluster size estimated from Raman values (Figure 3.5.5). It is interesting to note the decrease in $L_a$ over the series, suggesting a decrease in crystallite size. It is also noteworthy that the $L_a$ profile for the series resembles an exponential decay curve, which is expected as the introduction of oxygen functionalities fragments crystallites into increasingly smaller regions. When comparing the values with the average sp$^2$ domain size presented in Section 3.3, the estimations for $L_a$(XRD) are much higher than the calculated $L_a$(Raman) of approx. 1.1 - 1.4nm. This shows that the disordered regions in the crystallite remain active when measuring crystallite size in XRD while not active in measuring sp$^2$ cluster size in Raman, which helps to explain the large differences between measured $L_a$ values in literature. Additionally, it is seen in the literature with XRD estimations rarely falling below 2 nm, even for the most disordered carbon materials. It is also suggested that the $L_a$(XRD) weights more heavily on the bigger crystallites when taking into account the effect of multi-grain sized system. It is also possible that the measured peak width is partially obstructed by the background present in amorphous materials artificially increasing the crystallite size. The peak assignments and FWHM for the 002, 100 and 110 peaks for the GO$_{MRHxx}$ Series can be found in the appendices (Table 10.2-1).
The estimated crystallite thicknesses are also included in Figure 3.5.5. It shows a decrease in thickness from the starting material to GO\textsubscript{MRH12}, and then a small increase, followed by a plateau. The initial decrease is expected as a result of the oxidation process breaking up the ABA layering of the starting material. The increase in thickness between GO\textsubscript{MRH12} and GO\textsubscript{MRH13} can be explained based on the change in interlayer distance, which occurs at this transition as signified by the increase in d spacing associated with the 002 peak. Therefore, while the thickness has increased, the number of layers has remained similar. Finally, the plateau is seen as analysis was taken in powder form, thus limiting the separation of exfoliated flakes. In conclusion, from the XRD data it is possible to see an increasing trend in the interlayer distance with oxidation, as the sheets are separated by the introduction of oxygen functionality, and a decrease in the average crystallite size, providing evidence that the addition of these oxygen functionalities causes defects in the graphitic lattice. These defects are known to have serious repercussions on the electrical properties of the GO layers.\textsuperscript{58}

3.6 Characterisation of Graphene Oxide Materials via UV-Vis
To probe the optical absorption properties, including the optical band gap of the GO samples, Ultra violet – visible light spectroscopy (UV-Vis) is used, which as a technique is
explained in more detail in Section 2.3.4. UV-vis absorption spectra (185–750 nm, 0.5 nm resolution) were acquired using UV-vis spectroscopy (Varian Cary 5000 UV-vis-NIR absorption spectrometer, Agilent Technologies, USA), utilizing quartz cuvettes with optical path lengths of 10 mm. It is noted that there is no visible trace of residual unreacted KMnO$_4$ in any of the GO$_{HMx}$ or GO$_{MRHxx}$ samples as detectable by UV-Vis spectroscopy. Trace unreacted KMnO$_4$ would show a peak in the 400 – 500 nm range of the spectra. The lack of peak in this region shows no residual KMnO$_4$ is present, showing that the washing step in the original synthesis is effective. The GO solutions measured are prepared as previously described in Section 3.3.

UV-Vis absorption spectra of aqueous GO solutions for the GO$_{HMx}$ series are presented in Figure 3.6.1. There are two distinct features present in all the spectra for this series. Firstly, a peak occurs at approximately 230 nm (5.4 eV) which corresponds to the $\pi - \pi^*$ transition for aromatic C = C bonds present in the GO structure.$^{148}$ The second feature is the characteristic shoulder peak at approximately 300 nm (4.3 eV) which corresponds to the $n - \pi^*$ transition. This shoulder is commonly assigned to either C – O – C bonds$^{148}$ or C = O bonds$^{149}$ and therefore provides evidence for oxygen functionality on the GO sheets.$^{148,149}$ Comparing the spectra of the GO$_{HMx}$ series, it is clear that the peak positions are comparable, with some small variation in absorption intensities. These variations in absorption intensities are likely the result of slight measurement differences likely caused by small variations in analyte concentration. It is possible the variations point to small increases in disorder, possibly the result of a higher quantity of disordered GO flakes remaining in solution. Overall, the GO$_{HMx}$ series shows that increasing amounts of GO can be synthesised without making significant changes to the UV-visible absorption properties.
In the normalised absorption spectra for the GO\textsubscript{MRHxx} series, (Figure 3.6.2), the peak at 230 nm and the shoulder at 300 nm are present in the second half of the series (GO\textsubscript{MRH14} - GO\textsubscript{HRM16}) similar to the GO\textsubscript{HMx} series. The beginning of the series (GO\textsubscript{MRH11} - GO\textsubscript{MRH12}) shows a small peak at 275 nm (4.5 eV), which is similar to that of some rGO materials presented in literature.\textsuperscript{150} This peak shifts towards the 230 nm peak present in the latter half of the series. This is further evidence of sp\textsuperscript{2} carbon atom conversion into sp\textsuperscript{3} carbon atoms, resulting in the loss of some of graphite’s delocalised π molecular orbitals. It should also be noted that the solution changes from black to yellow - brown colour upon oxidation in the series. This occurs because the sp\textsuperscript{2} structure of graphite provides a wide range of conjugation lengths, which allow for absorption across a broad range of the spectrum. As oxidation progresses, sp\textsuperscript{2} atoms are converted to sp\textsuperscript{3} atoms which lowers the average conjugation lengths, shifting the absorption peak position to the lower wavelengths and increasing the optical band gap. This division of large conjugates into multiple small conjugates greatly affects the intensity of the absorption bands, leading to an increase in relative absorption in the lower wavelength region.
The content of sp\(^3\) carbon atoms increases across the series as the materials change from an unoxidised state to that of a fully oxidised GO state. By laying out the UV-vis data GO\(_{MRHXX}\) series as Tauc plots it is possible to estimate the optical band transitions for the series and estimate the optical band gap (Figure 3.6.3). The optical band gaps show an increase across the first half of the series, from 1.03 eV to 3.41 eV for GO\(_{MRH11}\) to GO\(_{MRH14}\) respectively. It is suggested that this is caused by the π – π* transition in sp\(^2\) carbon atoms. This clearly indicates a loss in sp\(^2\) content, as delocalised π orbitals near the Fermi level are removed, resulting in an enlarging of the optical band gap. The optical band gaps for the latter part of the series show signs of plateauing, suggesting that the sp\(^3\) content and subsequently disorder have reached a maximum possible level without the material breaking down completely. This is in agreement with the TGA and Raman analysis in Section 3.3 and Section 3.4 (Figure 3.6.4). It is interesting to note that the band gap for GO\(_{MRH13}\) of 2.03 eV is much lower than the plateauing values of the latter part of the series (3 - 3.42 eV) despite the fact that the XRD data suggests that GO\(_{MRH13}\) has a much larger interlayer distance, and
therefore should be much easier to exfoliate. This suggests that the increase in interlayer distance happens before plateauing in band gap, demonstrating the possibility for decreasing disorder without sacrificing solution process-ability.

![Tauc plots for the GO\textsubscript{MRH\text{XX}} series, the dashed red lines show the lines used to extrapolate the band gap ($E_g$) from each plot. An $r$ value of 0.5 is used to determine the direct optical band gap of the samples.](image)

**FIGURE 3.6.3** Tauc plots for the GO\textsubscript{MRH\text{XX}} series, the dashed red lines show the lines used to extrapolate the band gap ($E_g$) from each plot. An $r$ value of 0.5 is used to determine the direct optical band gap of the samples.

![Calculated optical band gaps for the GO\textsubscript{MRH\text{XX}} series compared against the thermal decomposition temperature in air measured using TGA, and the FWHM of the D peak measured using Raman. GO\textsubscript{MRH10} is included with a band gap of 0.02 eV.](image)

**FIGURE 3.6.4** The calculated optical band gaps for the GO\textsubscript{MRH\text{XX}} series compared against the thermal decomposition temperature in air measured using TGA, and the FWHM of the D peak measured using Raman. GO\textsubscript{MRH10} is included with a band gap of 0.02 eV.

It is interesting to note that the latter half of the series shows prominent additional lines which could be used to extrapolate another band transition (as shown in blue). This transition has an energy of approximately 4.2 - 4.5 eV which is significantly higher than the $\pi$
- $\pi^*$ transition at 3.4 eV. It is possible that this is the $n-\pi^*$ transition as a result of $C=O$ and $C-O-C$ bonds present in regions of disorder. The transition is also seen in measurements using photoluminescence spectroscopy as shown in Figure 3.6.5.

The photoluminescence for GO shows the presence of 3/4 distinct bands, a broad band which peaks at approximately 2.4 eV, which is attributed to localised states caused by water trapped between layers of GO. This band can be significantly decreased with annealing at temperatures as low as 50°C. The next two peaks, situated at approximately 3.1 eV and 3.5 eV could be both caused by the $\pi-\pi^*$ transition, as a range of different isolated sp$^2$ cluster sizes would result in different band transition energy for each cluster and subsequently the appearance of multiple peaks. This would match with the band gaps estimated for GO$^{\text{MRH14}}$, GO$^{\text{MRH15}}$ and GO$^{\text{MRH16}}$ via the Tauc plots. The final band peaks at approximately 4.2 eV is similar to the additional lines extrapolated from the Tauc plots for the GO$^{\text{MRHn}}$ series and the $n-\pi^*$ transition. It is proposed that because the $n-\pi^*$ transition
only occurs in regions of high disorder, the energy lost through non-radiative transitions i.e. the difference between absorption (as measured by UV-Vis) and emission (as measured by PL), is very small as a result of short conjugation lengths in disordered region. It is also possible that this is also caused by the distribution of very small sp² cluster sizes, resulting in further broadening of the π - π* band. This matches with calculated values for the π - π* transition which suggest an sp² cluster containing only 2 aromatic rings would have a π - π* transition energy of 4.2 eV.¹⁵²

In conclusion, UV-visible spectroscopy can be used to estimate the optical band gap of the GO materials; which is a direct measure of the degree of delocalised π bonding and therefore relates to the amounts of sp² and sp³ carbon atoms. Using this technique, it is shown that the GO_{MRHxx} series increases in band gap until it reaches a maximum value of approximately 3.4 eV, where it reaches a stable maximum sp³ content without breaking down completely. While the optical band gap of GO materials is shown to be tuneable between 1 – 3.4 eV, the interlayer distances suggested by XRD suggest that only GO_{MRH13} and higher will be solution process-able, limiting the tuneable band gap region to 2 - 3.4 eV for a solution process-able material. The Tauc plots and PL do suggest that this region could be increased by further reducing the size of sp² domains. The Tauc plots and PL also show evidence for variation in the sp² cluster size, resulting in separate bands in the band structure.

**FIGURE 3.6.6 SCHEMATIC REPRESENTATION OF THE π BAND STRUCTURE FOR GO_{MRH11} AND GO_{MRH16} SHOWING THE DIFFERENCES IN BAND GAP (AS MEASURED BY TAUCE PLOTS AND PL) AND DIFFERENCES IN π - π* TRANSITION (AS MEASURED BY PEAK MAXIMA POSITION IN UV-VIS).**
3.7 CHARACTERISATION OF GRAPHENE OXIDE MATERIALS VIA FTIR

To investigate the oxygen functional groups present on GO, and determine whether certain functional groups form preferentially when compared with others, the infrared absorption of GO materials were analysed. Fourier transform infrared spectroscopy (FTIR) spectra (4000 – 350 cm\(^{-1}\), resolution 2 cm\(^{-1}\)) were measured using an FTIR spectrometer (Varian Cary 660 FTIR spectrometer). Samples were measured for attenuated total reflectance (ATR) using an ATR attachment. The FTIR spectra for the GO\(_{HMx}\) series are presented in Figure 3.7.1. The characteristic peaks for GO as defined in literature include a broad peak at approximately 3400 cm\(^{-1}\), which can be attributed O-H stretching vibrations. This suggests the presence of alcohol functional groups and/or the presence of water molecules in the sample. The peaks at 1725 and 1618 cm\(^{-1}\) are assigned to C=O stretching vibrations, from carbonyl and carboxylic groups, and the C=C aromatic rings present in the graphitic skeleton respectively. A slight peak can be seen at approximately 1225 cm\(^{-1}\), which can be attributed to C-OH stretching vibrations, and a final peak is visible at 1049 cm\(^{-1}\), which is attributed to C-O stretching vibrations of epoxy or alkoxy groups. Models of GO in the literature suggest that GO is made up of a variety of oxygen containing functional groups, including alcohols, carboxylic acids, and epoxides.\(^{46}\) One of the limitations to infrared spectroscopy is the inability to accurately determine the amount of each functional group present. Therefore, it can only be used to confirm the presence or absence of functional groups. In the GO\(_{HMx}\) series, all 3 samples show the characteristic peaks for GO, indicating GO has been synthesised. The scale up series show that there are no peaks lost or gained, indicating that there is no change in the variety of functional groups present with scale up.
The FTIR spectra for the GO<sub>HMX</sub> series are presented in Figure 3.7.2. The major peaks visible in the GO<sub>HMX</sub> series are also visible in the GO<sub>MRHxx</sub> series. This includes the major peaks at 1725 and 1618 cm<sup>-1</sup>, the slight peak at 1225 cm<sup>-1</sup>, and final peak at 1049 cm<sup>-1</sup>, showing the same functional groups present throughout the series. The only peak with a visible variation is the broad peak at 3400 cm<sup>-1</sup>, which is greatly reduced for both GO<sub>MRH11</sub> and GO<sub>MRH12</sub>. By comparing these FTIR results with the XRD results presented in Section 3.5, it can be seen that the broad 3400 cm<sup>-1</sup> peak which is indicative of O – H bond stretches, only occurs in samples with an XRD peak at approximately 10<sup>5</sup>, corresponding to an interlayer distance of 8 – 10 Å. This would suggest that the oxidation process separates the layers, allowing water to penetrate between the layers. This explains why GO materials are soluble in water while other more graphitic materials are not. The presence of water trapped between the layers is also seen in the TGA results presented in Section 3.4. The GO<sub>MRHxx</sub> series therefore shows that similar functional groups have been formed throughout the series, however the amount of oxidation in the series will affect the presence of water trapped in between the layers, as shown by TGA analysis, dependant on the interlayer distance determined from the XRD results.
FIGURE 3.7.2 FTIR SPECTRA FOR THE GO$_{\text{MRHxx}}$ SERIES. ALL MAJOR PEAKS HAVE BEEN HIGHLIGHTED WITH DOTTED LINES, THE PEAK AT APPROXIMATELY 2300 cm$^{-1}$ IS ATTRIBUTED TO ATMOSPHERIC CO$_2$ AND THEREFORE NOT CONSIDERED.

3.8 SUMMARY

In this chapter, the synthesis of GO was investigated through various spectroscopic methods. The scalability of GO was investigated through the GO$_{\text{HMx}}$ series, and it was concluded that variations in batch size for the Hummers’ method show no visible difference measureable by the spectroscopic techniques used, when the reaction conditions are kept constant. This suggests that scaling of the Hummer’s method is possible without compromising material quality.

The GO$_{\text{MRHxx}}$ series demonstrates that, by increasing the quantity of KMnO$_4$ in the synthesis method, variations can be made on the final GO product. Primarily, this is the result of oxygen functionality being added, as shown by the increase in yield throughout the series, and confirmed by FTIR measurements. However, the addition of this oxygen functionality onto sp$^2$ carbon atoms results in an increase in disorder, as sp$^2$ carbon atoms in the lattice are converted into sp$^3$ carbon atoms. At first, this leads to a decrease in the sp$^2$ cluster size, as measured using the Raman I$_D$/I$_G$ ratio, and the creation of sp$^2$ carbon chains, resulting in a shift in the Raman G peak position. These sp$^3$ chains are subsequently targeted by further oxidation leading to the isolation of individual sp$^2$ carbon domains. The isolation of sp$^2$ clusters results in a splitting of the band structure, as demonstrated by UV-Vis Tauc plots and confirmed using PL spectroscopy.
Increasing the disorder around an isolated sp² cluster results in an increase in stress applied to the sp² cluster, due to the transition from trigonal planar sp² to tetrahedral sp³ bonded carbon atoms. This increase in stress results in a broadening of the Raman D and G peaks (Section 3.3). The increased disorder also causes a decrease in oxidative stability as measured by the thermal decomposition temperature in air (Section 3.4) and a decrease in band gap as measured by UV-Vis (Section 3.5). These parameters can therefore be used as a measure of disorder in further studies. Further oxidation causes an increase in disorder, without further reducing the average sp² cluster size causing the I_D/I_G ratio to stay the same, while overall disorder increases. This is caused by a reduction in overall sp² sites, lowering both the D and the G peaks simultaneously. An increase in disorder and its effect on sp² cluster size is demonstrated schematically in Figure 3.8.1. It is therefore shown to be unreasonable to only report the I_D/I_G ratio as a figure of merit when discussing the disorder associated with a GO material as is common in literature.

Out of the plane, XRD results show that an increase in the interlayer distance occurs with increasing oxidation, resulting in the d spacing rising from 3.4Å to approximately 8-10Å. This allows the inclusion of water in between the layers which will likely aid exfoliation and greatly increasing surface area. This is important for future use in applications discussed in subsequent chapters (Primarily Chapter 7).
4 THE SYNTHESIS AND CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS

4.1 INTRODUCTION
In this chapter, a variety of environmentally friendly reduction methods are used to reduce GO to rGO. The output of each reduction process is determined by characterising the quality of the final product and benchmarking against standards. This is achieved using a variety of techniques including: Raman spectroscopy (Section 4.3); thermogravimetric analysis (Section 4.4); X-Ray diffraction (Section 4.5); ultra-violet visible spectroscopy (Section 4.6); and Fourier transform infrared spectroscopy (Section 4.7). The results of these techniques are compared with the figures of merit reported in Chapter 3 and used to determine the disorder and oxygen functionality present in the material produced. The novel hybrid material, rGO with iron nanoparticles (Fe-rGO), is also introduced in this chapter, and characterised using the techniques listed above. The trends shown for GO and rGO materials are then used to determine the quality of the Fe-rGO material. The overall aim of this chapter is to determine how different reduction methods affect the rGO material produced, allowing for the best rGO material to be used for specific applications.

4.2 SYNTHESIS OF REDUCED GRAPHENE OXIDE BASED MATERIALS
GO was reduced in a variety of different ways to create 3 different rGO materials, labelled as the following: thermally annealed reduced (rGO\textsubscript{TA}), solar reduced (rGO\textsubscript{Sol}) and vitamin C reduced (rGO\textsubscript{VC}). A nanoparticle hybrid combining rGO with encapsulated iron nanoparticles is also synthesized which is labelled as Fe-rGO. For rGO\textsubscript{TA}, the GO solution was spray coated onto glass substrates and subsequently heated to 250°C, which was determined to be higher than the reduction temperature determined in Section 3.4. These films were used for UV-Vis, Raman and FTIR measurements. For XRD and TGA analysis, GO powder was heated to 250°C for 1 hour in air using a Heraeus UT6060 oven. This powder was also analysed with Raman to ensure similarity with the deposited thin films. For rGO\textsubscript{Sol}, the reduction was achieved by placing GO powder under a converging lens in direct sunlight, causing a photo-thermal reduction and exfoliation.\textsuperscript{153} This reaction is similar to thermal annealing as the temperature is measured to reach as high as 300°C at the focal point.

For rGO\textsubscript{VC}, 100 mL of GO solution was prepared at 2 mg/mL concentration in water, prior to addition of vitamin C (200 mg). The mixture was then heated to 80°C for 1 hour to ensure
sufficient reduction. Raman spectroscopy was used to confirm that the reduction was taken to its completion as shown in Section 4.3. This complete reduction resulted in the formation of a black precipitate which was dried to give rGO<br>powder, which was used for Raman, UV-Vis, FTIR, XRD and TGA comparison.

A novel hybrid rGO material, Fe-rGO, was synthesised by the incorporation of iron nanoparticles via a modified Pechini method. In brief, highly concentrated GO solution (25 mg/mL, 40 mL) is mixed with an iron based resin. To make the resin, citric acid (6 g) is dissolved in water (40 mL), followed by the addition of iron (III) nitrate nonahydrate (8 g). The citric acid acts as chelating agent, by forming metal citrate ions. Ethylene glycol (60 mL) is then added and the resulting mixture is heated to 80°C while stirring. This causes a polyesterification to occur between the metal citrate and the ethylene glycol forming a metallic polymer. Upon reaching 80°C, the mixture is placed in a bath sonicator for 30 minutes to ensure a homogeneous dispersion. This process of heating to 80°C then sonicating is repeated 3 times. At this point the resin is mixed with the highly concentrated GO solution, heated to 80°C and sonicated as before. The heating and sonication steps are repeated again to ensure complete mixing of the GO solution and the iron resin. At this point, the mixture is filtered under vacuum and dried in a vacuum oven at 50°C for 12 hours. It is important to note that the material is not rinsed prior to drying as this would remove the resin from the GO surface. Once the material is dry, it is transferred into a crucible which is placed in a tube furnace under nitrogen and heated to 850°C for 2 hours (10°C/min heating rate). This high temperature is required to turn the iron resin into iron nanoparticles, while simultaneously reducing GO to rGO as demonstrated by TGA data presented in Section 3.4. The reaction is conducted under nitrogen to avoid the thermal decomposition of GO (Figure 3.4.2). The resulting material is decorated with iron nanoparticles, resulting in the material being susceptible to magnetic fields. This is demonstrated in Figure 4.2.1.
FIGURE 4.2.1 DIGITAL PHOTOGRAPHS OF Fe-rGO IN SOLUTION, WITH AND WITHOUT THE APPLICATION OF AN EXTERNAL MAGNETIC FIELD (APPLIED USING 6 SMALL BALL MAGNETS). THE INSET SHOWS A TEM IMAGE OF AN IRON NANO PARTICLE IN Fe-rGO WITH A VISIBLE IRON CORE SURrounded BY A GRAPHITIC OUTER LAYER. (IMAGES COURTESY OF N. L. V. CARREÑO, FEDERAL UNIVERSITY OF PELOTAS, PELOTAS, BRAZIL)

4.3 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA RAMAN

To estimate the extent at which different reduction methods cause disorder, rGO samples were measured using Raman spectroscopy. All Raman examinations were conducted using a Renishaw 2000 microRaman spectrometer using the same experimental conditions as detailed in Section 3.3. To ensure the successful reduction of GO using vitamin C, Raman measurements were taken periodically, as a sample of GO was heated to 80°C in the presence of vitamin C. The details of this analysis are presented in Figure 4.3.1. The vitamin C process shows a sharp increase in I_D/I_G ratio, followed by a plateau which is reached after 10 minutes of heating. This is mirrored in the broadening of the peak widths which show a sharp decrease prior to plateauing. The reasoning for this plateau is unclear. It is possible that the vitamin C has reduced all available sites, resulting in the end of the reaction. It is also possible that the reduction has progressed far enough to affect the solubility of the GO, causing visible aggregation which limits the vitamin C’s ability to reduce the entire surface. Addition of further quantities of vitamin C do not result in a change the plateau, which demonstrates that the limiting factor is not quantity of vitamin C. For this work, the plateau reached in vitamin C reduction is considered the end of the reduction process.
Comparing the rGO materials against the trends seen for the GO materials allows some quantification of the quality of the rGO materials produced, in particular with regards to sp$^2$ carbon domain size and disorder content. In this section, each rGO material will be examined against the conclusions given in Section 3.3, to determine the validity of the trends when applied to rGO materials as well as GO materials. The Raman spectra for rGO$_{TA}$, rGO$_{VC}$, rGO$_{Sol}$ and GO, as a comparison, are presented in Figure 4.3.2 with the key characteristics detailed in Table 4.3-1.

### Table 4.3-1 D/G Peak Analysis for the rGO Samples Presented in This Thesis.
The average characteristics for the GO$_{HMX}$ are presented as a comparative reference.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak Position (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>D/G Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>D Peak</td>
<td>G Peak</td>
<td>D Peak</td>
</tr>
<tr>
<td>GO$_{HMX}$</td>
<td>1356 ± 3</td>
<td>1590 ± 3</td>
<td>118 ± 6</td>
</tr>
<tr>
<td>rGO$_{TA}$</td>
<td>1359 ± 1</td>
<td>1595 ± 1</td>
<td>109 ± 16</td>
</tr>
<tr>
<td>rGO$_{VC}$</td>
<td>1349 ± 1</td>
<td>1588 ± 1</td>
<td>66 ± 6</td>
</tr>
<tr>
<td>rGO$_{Sol}$</td>
<td>1365 ± 1</td>
<td>1584 ± 2</td>
<td>168 ± 2</td>
</tr>
</tbody>
</table>
All of the Raman spectra show the 5 characteristic peaks for GO/rGO materials. The Raman spectra for rGO$_{TA}$ shows a slightly lower $I_D/I_G$ ratio (0.73 ± 0.03) to that of the GO$_{HMx}$ reference (0.79 ± 0.10), however the intensity of the 2D, D+G and 2D’ peaks are somewhat lower. Utilising the equations presented in Section 3.3, the lower ratio of 0.72 is equated to an average sp$^2$ cluster size of 1.15 nm based on the equation for Region 1. As previously discussed, Region 1 is assumed where $I_D/I_G \propto L_a^2$ based on the FWHM of the D and G peaks which are both above 40 cm$^{-1}$ and therefore the $I_D/I_G$ ratio cannot be used in conjunction with the TK equation in Region 2 where $I_D/I_G \propto 1/L_a$. While the reduction in average cluster size for rGO$_{TA}$ initially suggests an increase in disorder, this is not the case, as the thermal reduction process results in the formation of new small sp$^2$ domains which lower the average sp$^2$ cluster size. This is reflected in the FWHM$_D$ of 109 ± 16 cm$^{-1}$ and FWHM$_G$ of 67 ± 3 cm$^{-1}$, which are both lower than their respective counterparts from the GO$_{HMx}$ series. This indicates that there is less disorder present in the sample.

The position of the G peak shifts from 1590 ± 3 cm$^{-1}$ to 1595 ± 1 cm$^{-1}$ when thermal reduction at 250°C is applied. As previously discussed in Chapter 3, a shift in G peak position towards 1615 cm$^{-1}$ is indicative of an increase in sp$^2$ carbon chains not present in aromatic rings. Therefore, it can be assumed that the thermal reduction process at 250°C results in
the reformation of sp\(^2\) chains from disorder regions as well as forming new small sp\(^2\) clusters. This formation of sp\(^2\) chains and clusters eventually form a percolating network, connecting isolated sp\(^2\) clusters and re-establishing electrical conductivity through the material. This conclusion strongly agrees with models suggested in the literature regarding the thermal reduction of GO and its subsequent electrical properties.\(^{155}\)

Similarly, \(\text{rGO}_{\text{VC}}\) shows a decrease in peak broadening indicative of a lessening in disorder. The narrowing of the D and G peaks is significant with FWHM\(_D\) and FWHM\(_G\) values of 66 ± 6 cm\(^{-1}\) and 59 ± 4 cm\(^{-1}\) respectively, which is narrower than values found in \(\text{GO}_{\text{MRH11}}\). However, the \(I_D/I_G\) ratio of 1.17 ± 0.02 suggests an increase in the average sp\(^2\) cluster size to an estimated value of 1.45 nm which suggests that the reduction is increasing the size of sp\(^2\) clusters. While the position of the G peak for \(\text{rGO}_{\text{VC}}\) is found at 1588 ± 2 cm\(^{-1}\), a shoulder can be seen forming at 1615 cm\(^{-1}\) as shown in Figure 4.3.3. This shows that the vitamin C reduction not only increases the size of sp\(^2\) clusters, but also shows an increase in sp\(^2\) carbon chains when compared with GO, leading to the connectivity between sp\(^2\) regions, and subsequently electrical conductivity through individual sheets.

**FIGURE 4.3.3 Raman Spectra of the G Band Region for rGO Samples, Highlighting the Partial Resolution of the G and D’ Peaks Seen for \(\text{rGO}_{\text{VC}}\)**
Similar to rGO\textsubscript{TA}, rGO\textsubscript{Sol} exhibits an \( I_D/I_G \) ratio of 0.73 ± 0.02, which corresponds to an average sp\(^2\) cluster size of 1.15 nm when equated using the equations for Region 1 (\( I_D/I_G \propto L_s^2 \)). However, in contrast to rGO\textsubscript{TA}, rGO\textsubscript{Sol} shows significant D and G peak broadening with FWHM\(_D\) and FWHM\(_G\) values of 168 ± 2 cm\(^{-1}\) and 84 ± 1 cm\(^{-1}\) respectively. These values are very high, significantly higher than rGO\textsubscript{TA} and even higher than the parent GO material used. According to the disorder model established for the GO\textsubscript{MRHxx} series, this would suggest that disorder for rGO\textsubscript{Sol} has increased. This is reasonable to conclude, due to the erratic nature of the solar reduction process used. It is very likely that variations in temperature caused by the converging lens results in damage to the sp\(^2\) carbon network as well as removing oxygen functionality. This could lead to disorder in the form of dangling carbon bonds, as well as more extreme rip and tear type defects as seen in some thermally annealed rGO samples\(^{53}\).

The Raman spectra for Fe-rGO is presented in Figure 4.3.4 and compared to both GO and rGO\textsubscript{TA}. As the synthesis method requires heating at 850°C in nitrogen for the synthesis of Fe-rGO it is most comparable with rGO\textsubscript{TA}, as Figure 3.4.2 demonstrated very little difference in the TGA data after 300°C while heated under nitrogen. The \( I_D/I_G \) ratio for Fe-rGO is shown to be 0.81 ± 0.02, which is higher than rGO\textsubscript{TA}. This would equate to an average sp\(^2\) cluster size of 1.20 nm for Region 1 and approximately 11 nm for Region 2. While the FWHM\(_D\) and FWHM\(_G\) of 137 ± 6 cm\(^{-1}\) and 76 ± 1 cm\(^{-1}\) respectively would suggest Region 1 applies, it is possible that the addition of the iron nanoparticles results in additional internal stress on the sp\(^2\) lattice leading to increased peak broadening. The TEM image of Fe-rGO shown in Figure 4.2.1 (from the previous section) show the nanoparticles possess an iron rich core, surrounded by a graphitic carbon layer. This graphitic carbon layer could either be a complete graphitic layer grown around the iron nanoparticle, or more likely a stack of rGO layers forming an overlapping “onion-like” layered coating. Either of these cases could result in increased internal stress on the sp\(^2\) clusters. The position of the G peak also shifts down to 1584 ± 2 cm\(^{-1}\), which is lower than both rGO\textsubscript{TA} and GO. It is possible that the increased temperature allows for conversion of the sp\(^2\) chains formed at 250°C to be converted to aromatic sp\(^2\) regions, this would also lead to the increases in \( I_D/I_G \) ratio. Conversely, the G peak position, coupled with the FWHM\(_D\) and FWHM\(_G\) could be evidence of increased disorder similar to the rGO\textsubscript{Sol}.\(\)
FIGURE 4.3.4 RAMAN SPECTRA FOR Fe-rGO WITH THE RAMAN SPECTRA OF GO AND rGO_TA SHOWN AS COMPARISON REFERENCES.

By analysing the $I_D/I_G$, FWHM$_D$, and G peak position of all the rGO materials, it can be concluded the solar photo-thermal reduction method cause further disorder to the structure of the material more than the original oxidation process, while the thermal and vitamin C chemical reduction method go towards restoring the graphitic structure. This does not mean that rGO$_{VC}$ or rGO$_{TA}$ do not cause defects and disorder of their own, rather that the sp$^2$ content restored is significant enough to result in observable differences in the Raman spectra. This agrees with the results presented in the literature, specifically the mechanism for vitamin C reduction which suggests restoration of C=C bonds via vitamin C reduction. It is therefore theorised that rGO$_{VC}$ and rGO$_{TA}$ films may have an improved performance, when compared with pristine GO and rGO$_{Sol}$ in electronic applications which require properties such as film conductivity (see Chapter 6.3 for further investigations). This analysis also suggests that the common method of looking at the $I_D/I_G$ ratio as a way of determining degrees of disorder in graphitic structure can be supplemented by examining the broadening of the D and G peaks when fitted with a Lorentzian peak. This is useful in GO/rGO materials where small changes in the average sp$^2$ cluster size are difficult to resolve in the $I_D/I_G$ ratio, but are much clearer when the FWHM$_D$ and FWHM$_G$ are examined. This is shown in Figure 4.3.5 which compares the $I_D/I_G$ ratio, FWHM$_G$ and FWHM$_D$ of all GO and rGO materials produced. The shape of the $I_D/I_G$ vs FWHM$_D$ and the $I_D/I_G$ vs FWHM$_G$ plots are expected as it relates to the average sp$^2$ cluster size. Similar observations are seen for
samples of amorphous carbon as shown in the inset graph, and subsequently used to
discern the trend lines shown in blue.\textsuperscript{119} Pristine graphite has a low $I_D/I_G$ ratio because it has
a much large average sp\textsuperscript{2} cluster size, placing it firmly in the Region 2 of the graph shown in
the Figure 4.3.6. In contrast, the GO and rGO materials all have a proposed average sp\textsuperscript{2}
cluster size of less than 2 nm, placing it in Region 1 of the corresponding graph. Therefore, it
is concluded that for GO/rGO samples with average sp\textsuperscript{2} cluster sizes below 2 nm, the
FWHM\textsubscript{D} or the FWHM\textsubscript{G} are a good indicator of the disorder present and can be used to
estimate the extent of disorder of rGO samples. It is also concluded that rGO\textsubscript{VC}
demonstrates the least disorder, making it favourable for use in conductive thin film
applications. Without the use of the D and G peak widths, it would be very difficult to
determine from the $I_D/I_G$ ratio alone whether a material lies in Region 1 or Region 2 of the
graph presented in Figure 4.3.6.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure.png}
PLOTTED AGAINST THE LINewidth OF THE G PEAK FOR AMORPHOUS CARBON SHOWING THE EXPECTED SHAPE OF THE
CURVES TAKEN FROM LITERATURE (INSET REPRINTED WITH PERMISSION FROM REF 119. COPYRIGHT 1996 AMERICAN
INSTITUTE OF PHYSICS.)}
\end{figure}
4.4 CHARACTERISATION OF REDUCED GRAPHENE OXIDE MATERIALS VIA TGA

To further investigate the link between the thermal decomposition temperature in air and the disorder extent, rGO samples were measured using TGA. TGA was undertaken using a TA Instruments Q500 in air (balance gas, nitrogen: 40 cm$^3$ min$^{-1}$, sample gas, air: 60 cm$^3$ min$^{-1}$). Dried GO and rGO powders were placed on a platinum crucible and heated at a heating rate of 10 K min$^{-1}$, from room temperature to 900°C similar to the method described in Section 3.4.

To investigate the effect of thermal annealing on GO samples, multiple temperatures were applied. The temperatures were selected based on the mass loss steps presented in the GO TGA analysis (Section 3.4). The temperatures chosen were 50, 200 and 250°C. The TGA profiles for these temperatures are presented in Figure 4.4.1. As previously discussed, GO has three main mass loss regions, from 50 – 100°C, 150 – 300°C and 450°C+ respectively. It should be noted that all 4 plots show a degree of mass loss in the 50 - 100°C region. This mass loss step is likely due to evaporation of water adsorbed onto the surface from the

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**FIGURE 4.3.6 COMPARISON OF THE AVERAGE SP$^2$ CLUSTER SIZE ($L_a$) WITH RESPECT TO $I_D/I_G$ RATIO ACCORDING TO THE LITERATURE$^{140,156}$ WITH THE $I_D/I_G$ RATIOS AND CORRESPONDING $L_a$ VALUES SHOWN FOR rGO$_{vc}$, rGO$_{TA}$ AND rGO$_{sol}$**

To further investigate the link between the thermal decomposition temperature in air and the disorder extent, rGO samples were measured using TGA. TGA was undertaken using a TA Instruments Q500 in air (balance gas, nitrogen: 40 cm$^3$ min$^{-1}$, sample gas, air: 60 cm$^3$ min$^{-1}$). Dried GO and rGO powders were placed on a platinum crucible and heated at a heating rate of 10 K min$^{-1}$, from room temperature to 900°C similar to the method described in Section 3.4.

To investigate the effect of thermal annealing on GO samples, multiple temperatures were applied. The temperatures were selected based on the mass loss steps presented in the GO TGA analysis (Section 3.4). The temperatures chosen were 50, 200 and 250°C. The TGA profiles for these temperatures are presented in Figure 4.4.1. As previously discussed, GO has three main mass loss regions, from 50 – 100°C, 150 – 300°C and 450°C+ respectively. It should be noted that all 4 plots show a degree of mass loss in the 50 - 100°C region. This mass loss step is likely due to evaporation of water adsorbed onto the surface from the
atmosphere in the time between initial drying and analysis. It is much less pronounced for the 200 and 250°C samples where the hydrophobic nature of the rGO material decreases the propensity for water to be adsorbed onto the surface.

The second region (150 – 300°C) is proposed to be a combination of the removal of trapped water, and the removal of oxygen functionality involved in the thermal reduction processes. Both of these can be considered as irreversible processes, and therefore would not be present after annealing above the relevant temperature. This is supported by the TGA data for thermally annealed GO, specifically the thermal anneal at 250°C, which shows no mass loss step from 150 – 300°C, as the oxygen functionality and trapped water have both been removed by the previous thermal anneal. It is important to note that the 150 - 300°C mass loss step is still present after a thermal anneal at 200°C, signifying that not all the oxygen functionality / trapped water has been removed until 250°C has been applied. Finally, all thermally annealed samples show the last mass loss step starting at approximately 500°C with a derivative peak maximum at 600°C. This suggests that the extent of disorder is not changing with thermal annealing. This is in agreement with Raman data which shows little change in the I_D/I_G ratio and FWHM_D (discussed in Section 4.3) and is unsurprising as the thermal treatment required to reach 600°C is enough to reduce GO into rGO_TA regardless.
FIGURE 4.4.1 TGA PROFILES FOR GRAPHENE OXIDE THERMALLY ANNEALED AT 50, 200 AND 250°C TO FORM THERMALLY REDUCED GRAPHENE OXIDE (rGO$_{TA}$). THE DERIVATIVE WEIGHT LOSS IS SHOWN IN RED.

The TGA profiles for rGO$_{VC}$ and rGO$_{sol}$ are shown in Figure 4.4.2. For rGO$_{VC}$, similar to the GO thermally annealed at 250°C, the only prominent mass loss step is in the 450°C+ region as a result of the thermal decomposition in air to produce gaseous carbon by-products. The lack of prominent peaks before 450°C shows that most of the oxygen functionality / trapped water that can be removed via heating, have already been removed. There is a small mass loss gradient between 150°C and 300°C which could signify a small quantity of oxygen functionality / trapped water remains. The major mass loss step involves 80% of the mass being lost between 600 - 700°C. This is roughly 100°C higher than the thermal decomposition temperature for GO and rGO$_{TA}$. This indicates a lower degree of disorder for
rGO$_{VC}$ than GO and rGO$_{TA}$, which is in agreement with the Raman results presented in Section 4.3. In contrast, rGO$_{Sol}$ shows a much earlier thermal decomposition temperature losing approximately 80% mass at 350 - 430$^\circ$C. This indicates a much higher degree of disorder than rGO$_{TA}$, GO and rGO$_{VC}$, which is also in agreement with Section 4.3. It is interesting to note that the rGO$_{Sol}$ leaves a residue of approximately 15-20% after heating to 900$^\circ$C. The reason for this is currently unknown and would require further investigation to explain.

![TGA Profile](image)

**Figure 4.4.2 TGA Profile for Vitamin C Reduced Graphene Oxide (rGO$_{VC}$) and Solar Reduced Graphene Oxide (rGO$_{Sol}$). The derivative weight loss is shown in red.**

The TGA profile for Fe-rGO is presented in Figure 4.4.3. It is important to note that there is no mass loss from 0 - 400$^\circ$C. This is likely because in the Fe-rGO synthesis process the material is heated to 850$^\circ$C in a nitrogen atmosphere. As shown in Figure 3.4.2, a nitrogen atmosphere only stops the thermal decomposition into gaseous carbon materials from occurring. Therefore, the Fe-rGO material is comparable to the rGO$_{TA}$ and is expected to only lose mass after 400$^\circ$C when reacting with atmospheric oxygen as is the case. It is interesting to note that the thermal decomposition temperature for Fe-rGO is at approximately 400 – 500$^\circ$C. This is lower than GO, rGO$_{TA}$ and rGO$_{VC}$ and could signify a higher level of disorder in the Fe-rGO material. It could also be caused by interactions with the iron nanoparticles, lowering the rGO thermal decomposition temperature, however there is currently insufficient evidence to confirm whether this is occurring. After the thermal decomposition temperature, there is a residue of approximately 20% of the total mass left in Fe-rGO. It is proposed that the residue is caused by the iron nanoparticles present in Fe-rGO, as metallic iron has a melting point significantly higher than the temperature range used in the TGA analysis.
FIGURE 4.4.3 TGA PROFILE FOR REDUCED GRAPHENE OXIDE WITH IRON NANOPARTICLES (Fe-rGO). THE DERIVATIVE WEIGHT LOSS IS SHOWN IN RED.

By plotting the thermal decomposition temperature of all GO and rGO based materials discussed in this thesis against the corresponding Raman data, it is possible to estimate the extent of disorder produced by different reduction techniques by comparing with the previous estimations given in Section 4.3. This is shown in Figure 4.4.4, where the thermal decomposition temperature is compared to the \( I_D/I_G \) ratio \( FWHM_G \), \( FWHM_D \) and peak positions for the D and G peaks of all the materials studied. Comparing the thermal decomposition temperatures, with the figures of merit analysed using Raman spectroscopy for all the materials synthesised there is a clear order to the samples. The evidence suggests that the most disordered material produced in this investigation is the rGO_{sol} material while the least disordered material is the rGO_{VC} material. It is significant to note that the rGO_{sol} material is more disordered than even the most oxidized samples from the GO_{MRHxx} series, possibly as a result of the energetic nature of the solar reduction process.
In conclusion, the thermal decomposition temperature in air of GO and rGO samples show a strong correlation with the broadening of the D and G peaks measured by Raman spectroscopy. This confirms that the thermal decomposition temperature for GO/rGO samples is dependent on the degree of disorder present within the sample. Using the thermal decomposition temperature as a measure of disorder allows for the ordering of rGO samples in terms of disorder which can assist in forming a model for the oxidation and
reduction process. By plotting the thermal decomposition temperature against the G peak position, a two stage trend can be seen. Firstly, as disorder increases from GO to rGO$_{TA}$, the peak shifts up to 1595 cm$^{-1}$, moving towards the D’ peak typically given at 1615 cm$^{-1}$, signifying an increase in sp$^2$ chains as previously discussed. The second stage of the trend shows a decrease with further loss of disorder towards rGO$_{VC}$ and graphite. This is because the Raman D’ peak at 1615 cm$^{-1}$ for rGO$_{VC}$ is prominent enough to be counted as two separate peaks, therefore no longer affecting the position of the G peak, while pristine graphite will not have any sp$^2$ chains resulting in a lack of D’ peak entirely.

4.5 Characterisation of Reduced Graphene Oxide Materials via XRD

To understand the effect of GO reduction on the interlayer distance, and further characterise the rGO materials presented including Fe-rGO, rGO were measured using XRD. The Powder X-Ray diffractometer used for XRD analysis was a Panalytical X’Pert Pro with a copper x-ray tube and an incident beam graphite monochromator with Cu Kα radiation operating at 45 kV and 40 mA. Dried rGO powders were produced as detailed in Section 4.2 before being finely ground and used in sample preparation. The same experimental conditions used to analyse GO samples in Section 3.5 were used throughout this section.

The XRD profiles for the GO reduced via different methods are presented in Figure 4.5.1. All reduction methods display a broad peak at 24.3 ± 0.3°, corresponding to the 002 plane in graphitic materials, signifying an interlayer distance d spacing of 3.63Å. This is slightly wider than the interlayer spacing of the starting graphite powder calculated to be 3.35Å (Section 3.5). It is interesting to note that the GO reference sample shows a peak at 26.5°, similar to graphite but different to rGO. This shows that the as produced GO powder contains some residual unreacted graphite starting material originating from the original Hummer’s method. If this was simply reduced through the heating step of the Hummer’s method, the interlayer distance would be more in line with the rGO samples.
The rGO samples also contain a wider peak at 42 - 46°. The analysis of the GO_{MBHXX} series (Figure 3.5.4) showed that the 100 and 101 peaks are present at 42.6° and 44.4°, and with increasing oxidation and an expanding interlayer distance, the 101 peak begins to disappear. The rGO samples clearly show both the 100 and 101 planes are present, particularly in rGO_{TA} which is further evidence that the interlayer distance has been reduced with reduction. rGO_{TA} and rGO_{VC} both show presence of the final characteristic peak at 77.7° present in both GO and graphite samples. This corresponds to the 110 plane in graphitic materials. It is interesting to note that the 110 plane for rGO_{Sol} is not clearly visible, which could be another indicator showing that the solar reduction method has increased extent of disorder as a peak present in all samples including the starting graphite has been lost. This is likely because of the uneven nature of the solar reduction process.

The XRD pattern for the synthesised Fe-rGO material is presented in Figure 4.5.2. The major peaks present in Fe-rGO are at 26.10°, 35.47°, 43.19°, 44.57°, 64.86°, 77.80° and 82.19°. The peaks at 26.10°, 43.19° and 77.80° are also found in rGO and other graphitic materials and represent the 002, 100 and 110 planes for graphitic materials respectively. The peaks at 44.57°, 64.86° and 82.19° are characteristic of metallic iron and correspond to the 110, 200
and 211 planes for metallic iron respectively. The remaining peak at 35.47° is theorised to belong to a thin iron oxide shell surrounding the iron nanoparticle core. The exact composition of this iron oxide shell is difficult to determine, as both magnetite (Fe$_3$O$_4$) and maghemite (Fe$_2$O$_3$) have XRD peaks that could explain the peak at 35.47°. Both iron oxide materials have two main characteristic XRD peaks at around 35 and 63° corresponding to the 311 and 440 planes in the material both which could be argued as present in the Fe-rGO sample. Both magnetite and maghemite also shown magnetic properties which could add to the magnetism provided by the metallic iron core. By using the Scherrer equation on the 110 peak for metallic iron, (44.57°) the average diameter of the metallic iron core in the nanoparticles can be estimated as 24.8 nm. This is consistent with TEM images provided in Figure 4.2.1 (presented in Section 4.2).

**FIGURE 4.5.2 XRD PATTERNS FOR Fe-rGO (BOTTOM) COMPARED WITH rGO (MIDDLE) AND METALLIC IRON (TOP). THE METALLIC IRON COMPARISON PATTERN RUNS FROM 20 - 90° (REPRINTED (ADAPTED) WITH PERMISSION FROM REF 157 COPYRIGHT 2012 ROYAL SOCIETY OF CHEMISTRY.)**

### 4.6 Characterisation of Reduced Graphene Oxide Materials via UV-Vis

To determine the effect of reduction on the optical absorption properties, and estimate the band gap of rGO materials, rGO samples were measured using UV-Vis. UV-Vis absorption spectra (185–750 nm, 0.5 nm resolution) were acquired using UV-vis spectroscopy (Varian Cary 5000 UV-vis-NIR absorption spectrometer, Agilent Technologies, USA), utilizing quartz
cuvettes with optical path lengths of 10 mm as in Section 3.6. The analysis of rGO material using UV-Visible spectroscopy is complicated by rGO’s lack of dispersion properties in common solvents. The literature shows that it is very difficult to both disperse and exfoliate rGO powder in solvent, without the use of surfactants and exfoliating agents. For GO solutions, water is used as a solvent as it acts as both an exfoliating agent and a dispersing solvent. However, it is shown that when the reduction of GO occurs, the loss of the oxygen functionality on the surface reduces its hydrophilicity very quickly resulting in flocculation in aqueous solution. This can be seen in Figure 4.6.1, which shows digital photographs of the vitamin C reduction of GO in water to form rGO$_{VC}$. This reaction progresses much slower than the vitamin C reduction presented in Section 4.3 due to the lack of external heating, which has the advantage of making the reaction more controllable. It is clear that, as the reaction occurs, the brown GO solution turns into a black rGO solution, which then progressively flocculates into small flocs as seen at 144 hours. This process is greatly accelerated with the addition of heat as previously discussed (Section 4.3). It is previously stated in literature that the reduction of GO using vitamin C does not lead to agglomeration of particles, as it is suggested that the vitamin C breaks down into guluronic acid and oxalic acid which disrupt the $\pi - \pi^*$ stacking required for agglomeration.$^{64}$ However, it is possible that the reduction undertaken in the literature was not allowed to progress as far, leaving enough oxygen functionality present to prevent agglomeration. It is also possible that the large volume of vitamin C used in the literature (10:1 vitamin C: GO w/w) may delay the agglomeration process. Regardless the agglomeration of rGO samples including rGO$_{VC}$ makes it difficult to produce stable solutions of rGO material.
This is reflected in the UV-vis spectra for the rGO materials produced (Figure 4.6.2). The UV-vis spectra for the rGO samples show a broad absorption across the entire visible spectrum, which explains the apparent colour change from brown to black. A slight peak can be seen at approximately 279 nm in all samples, however the overwhelming absorption across the whole spectrum makes it very difficult to estimate the band gap. The only visible differences between the rGO samples are seen in the UV absorption range (below 250 nm). This region is often disregarded as a wide range of functional groups can cause absorption at these low wavelengths. These include ketones, carboxylic acids, aldehydes, esters, and most importantly benzene rings, which could all contribute to variations in the final region. However, the lack of peaks in the rGO\textsubscript{TA} does suggest a lower amount of functional groups absorbing in this region.
From the Tauc plots for rGO materials (Figure 4.6.3), it is clear that there are a wide range of energy states present, as linear extrapolations from different sections of the curve led to a range of band energies. All rGO films show a band gap nearing 0 as highlighted by the red dashed lines. This is in agreement with band gap assignments made for few layer rGO via hydrazine reduction as measured using ellipsometry.\textsuperscript{159} The lessening of this band gap is an indicator of the sp\textsuperscript{3} to sp\textsuperscript{2} conversion which has occurred in all samples to some extent. It should be noted that rGO\textsubscript{Sol}, while closer to 0 than GO, still shows a gap of approximately 0.5 eV, which is higher than the other rGO samples. This is in agreement with the previous disorder studies which suggest that rGO\textsubscript{Sol} may contain higher quantities of disorder and defects, when compared with other rGO samples. The significant reduction in band gap between GO and all the rGO samples suggests that all the reduction methods tested restore some degree of conjugation between sp\textsuperscript{2} clusters resulting in a long sp\textsuperscript{2} conjugation length and subsequently lower band gaps.
FIGURE 4.6.3 Tauc plots for rGO\text{VC}, rGO\text{TA}, rGO\text{Sol} and Fe-rGO. The dashed red line is used to extrapolate the band gap, while the dashed blue lines represent other additional transitions. An r value of 0.5 is used to determine the direct optical band gap of the samples.

It should also be noted that all the rGO samples exhibit multiple additional lines which could relate to other transitions, specifically $\pi - \pi^*$ transitions of isolated sp$^2$ domains as shown in blue. The band transitions associated with the blue lines range from approximately 3.0 eV to as high as 5.9 eV. These are all within the range of $\pi - \pi^*$ proposed in literature for different size sp$^2$ domains. The presence of multiple lines in rGO\text{Sol} suggests a wide range of isolated sp$^2$ size domains in the structure, which suggests a higher degree of domain isolation than rGO\text{TA}. This data fits with conclusions relating to Raman, specifically that rGO\text{TA} results in the crosslinking of sp$^2$ regions, limiting the variety of isolated sp$^2$ cluster regions. Each of the rGO samples has a transition between 3.4 – 4.2 eV. It is possible that this is the result of n – $\pi^*$ transitions from residual oxygen functional groups similar to GO, with the added shift to lower energies caused by proximity to longer conjugation lengths, resulting in a spreading of the $\pi^*$ band.

It is possible that that values for the band gaps are artificially enlarged by the experimental set up. Owing to the lack of solubility for rGO products in water, it is possible that only flakes with high quantities of oxygen remaining are left in solution. This could result in higher concentrations of unreduced flakes in the sample making it not fully representative of the whole sample. It is however possible to conclude that the GO to rGO transition results a colour change from brown to black, which signifies a closing in the band gap caused by the
conversion of sp\(^3\) to sp\(^2\) carbon atoms. It is also clear that agglomeration occurs upon reduction, which demonstrates a reduction in the oxygen functionality changing the solubility properties through the course of the reduction, which can cause difficulty for solution processing applications.

### 4.7 Characterisation of Reduced Graphene Oxide Materials via FTIR

In order to determine whether different reduction methods target specific oxygen functional groups, rGO samples were measured using FTIR spectroscopy. FTIR spectra (4000 – 350 cm\(^{-1}\), resolution 2 cm\(^{-1}\)) were measured using an FTIR spectrometer (Varian Cary 660 FTIR spectrometer). Samples were measured for attenuated total reflectance (ATR) using an ATR attachment as in Section 3.7. The FTIR spectra for the rGO materials are presented in Figure 4.7.1 and Figure 4.7.2. The GO reference spectra shows a broad peak at 3400 cm\(^{-1}\), then peaks at 1725 and 1618 cm\(^{-1}\), a slight peak at 1225 cm\(^{-1}\), and final peak at 1049 cm\(^{-1}\). These peaks correspond to O–H, C = O, C – C, C – OH, and C – O bonds respectively as described previously (Section 3.7). The FTIR spectrum for graphite shows a lack of prominent features indicating the lack of functional groups present.

For the rGO materials, rGOT\(_\text{Aa}\), rGO\(_\text{Sol}\), rGO\(_\text{VC}\) and Fe-rGO, there are still small peaks visible at 1725, 1618 and 1225 cm\(^{-1}\) corresponding to the C = O, C – C and C – OH bonds. There is no sign of the peak at 1049 cm\(^{-1}\), signifying a loss of C – O bonds specifically associated with epoxide and alkoxy functional groups. It may be that this peak has been removed or significantly reduced in intensity so that it is now hidden by the 1225 cm\(^{-1}\) peak. As it is theorised that epoxide groups are present on the surface of the GO flakes, as opposed to the edges, this reduction in epoxide groups may help explain the decrease in interlayer distance demonstrated in the XRD analysis (Section 4.5). With a reduction in the amount of oxygen functionality between the layers, the rGO sheets can stack closer together, increasing the van der waals forces present, decreasing the interlayer distance and also increasing the chance of flocculation. This is seen in the dispersion studies in Section 4.6, and makes solution processing of rGO material very difficult. The presence of the broad peak at 3400 cm\(^{-1}\) is very difficult to discern because of the background absorption present. The large background absorption associated with rGO materials seen in UV-Vis makes it very difficult to determine much useful information from the FTIR data.
4.8 Summary

In summary, GO was reduced to form rGO in a variety of environmentally friendly ways. Reductions were carried out using both chemical (via vitamin C reduction) and thermal annealing, in the forms of low temperature thermal annealing (300°C) and photo thermal reduction using light and a converging lens. The materials produced were then compared with the GO materials produced in Chapter 3 using a variety of techniques. Raman analysis
of the I_d/I_g ratio, FWHM_G and FWHM_D, coupled with thermal decomposition temperature taken from TGA data were used as figures of merits to determine the disorder present in samples, as well as improve the way that rGO materials are assessed. XRD analysis, together with UV-visible data and FTIR data, are used to explain agglomeration and subsequently the lack of solution process-ability in rGO samples.

When GO is thermally annealed at 250°C, Raman results show a decrease in sp^2 cluster size, and yet a small reduction in disorder based on FWHM_D and FWHM_G which were shown to vary with increasing disorder in Chapter 3. This can be explained by the formation of new small sp^2 clusters which lowers the average sp^2 cluster size. rGO_TA also shows the Raman G peak shift towards the 1615 cm\(^{-1}\) position of the D’ peak, signifying an increase of sp^2 chains not incorporated in aromatic ring systems. These sp^2 chains allow for interconnection of sp^2 domains resulting in percolation and subsequent conductivity documented in literature.\(^{155}\) This connectivity between sp^2 regions results in a significant reduction in the band gap as measured by UV-Vis. With further reduction, these sp^2 chains will combine with pre-existing sp^2 clusters, increasing the average sp^2 cluster size as in rGO_VC. This process is represented schematically in Figure 4.8.1. The interconnected nature of the sp^2 clusters increases the overall conjugation length, resulting in a decrease in the band gap to nearly zero for all rGO samples as shown by Tauc plots.

A novel material was developed, incorporating iron nanoparticles into rGO. XRD analysis confirms the nanoparticles incorporate a 25 nm metallic iron core, with a thin layer of iron oxide (Fe_2O_3 or Fe_3O_4) surrounding the core. TEM images also show that these iron
nanoparticles are contained within a graphitic outer shell. The presence of the iron nanoparticles are expected to change the work function of the material, better suiting the deep HOMO levels of high efficiency active layer polymers. The Fe-rGO material is also shown to be magnetic, which is an advantageous property for future applications.
5 GRAPHENE OXIDE MATERIAL INTERFACES IN ORGANIC PHOTOVOLTAIC APPLICATIONS

5.1 INTRODUCTION
In this chapter, the methods for using GO materials as a HTL in OPV devices are detailed. Section 5.2 details the fabrication processes used to construct OPV test devices. The GO thin films are then characterised via SEM and AFM before use in OPV devices (Section 5.3). Section 5.4 presents OPV device performance characteristics and details GO deposition optimisation to achieve higher device performance. These devices are compared with devices with no HTL, and with devices with a PEDOT:PSS HTL. The effect of disorder, present in the GO material as a HTL, is also investigated using select GO materials from the GO\textsubscript{MRHxx} series as HTLs. Section 5.5 compares the lifetime performances of devices with a GO HTL against similar devices using a PEDOT:PSS HTL, both in air and under nitrogen storage conditions. This allows for the testing of degradation caused both by internal instability and external atmospheric influences. Section 5.6 compares the unilluminated current voltage relationships for devices with no HTL, with GO and with PEDOT:PSS to investigate the effect of the addition of the HTL on charge transport properties. Finally, the novel hybrid material, Fe-rGO, presented in Chapter 4 is utilised as a HTL in test devices, leading to promising enhancements in device performance. The overall aim of this chapter is to determine the extent to which GO materials can be used to improve the performance of organic photovoltaics.

5.2 MATERIALS AND METHODS FOR PRODUCING GRAPHENE OXIDE INTERFACIAL LAYERS IN ORGANIC PHOTOVOLTAIC
The Hummers method (Chapter 3) was used to make GO solutions, specifically the GO\textsubscript{HMx} series. This involved dispersing a set weight of GO powder in a set solution volume, and sonicating for 10 minutes using a probe sonicator (Cole-Parmer Ultrasonic Processor). To ensure no large clusters of unreacted material remained, the solution was then left to settle overnight (approx. 16h) and then the top layer decanted.

ITO on glass substrates (15 Ω/□), and Bathocuproine (BCP) were purchased from Luminescence Technology Corp (Taiwan). PEDOT:PSS (Clevios P VP Al 4083, Heraeus GmbH, Germany) was filtered (0.2 µm) before use. TiO\textsubscript{2} was produced using a previously reported
sol gel synthesis method followed by a 1:200 dilution of the sol gel product with methanol.\textsuperscript{160} Acetone and propan-2-ol (IPA) were purchased from Sigma Aldrich (UK).

For the imaging of films, scanning electron microscopy (SEM) images were acquired using a scanning electron microscope (FEI Quanta 200) under high vacuum. Atomic Force microscopy (AFM) images were taken using a Veeco Dimension 3100 in tapping mode.

For OPV testing purposes, PCDTBT:PC\textsubscript{70}BM solar cells were fabricated. Briefly, ITO on glass substrates were washed by sonicating in acetone and IPA for 10 minutes each. The dried ITO substrates were then subjected to an oxygen plasma treatment (Emitect K1050X 100W, 15 SCCM, 5 mins). This cleaning process was also used when depositing materials on silicon substrates. Aqueous GO solutions of various concentrations were deposited onto the ITO substrates to give optimised thin GO films. For a comparison reference, PEDOT:PSS was sonicated for 5 min before spin-coating (5000 rpm, 1 min) giving a 40 nm film. Both GO and PEDOT:PSS films were annealed (150-200°C) for 10 min. PCDTBT:PC\textsubscript{70}BM (1:4, 7mg/mL PCDTBT concentration) was dispersed in a solution of dichlorobenzene (DCB) and chlorobenzene (CB) (1:3). This was deposited via spin coating (5500 rpm) to give an approx. 70 nm film before annealing (80°C, 10 min), prior to depositing the electron transport layers. For TiO\textsubscript{x} devices, the TiO\textsubscript{x} precursor was spin-coated (5000 rpm, 1 min) on top of the PCDTBT:PC\textsubscript{70}BM layer, giving a 10 nm film, then annealed in air (80°C, 10 min). The film is annealed in air to allow for the formation of Ti – O – Ti linkages through hydrolysis and condensation resulting in a TiO\textsubscript{x} barrier network. For BCP devices, BCP was evaporated onto the PCDTBT:PC\textsubscript{70}BM giving a 5 nm layer. Finally, Al electrodes (100 nm thick) were deposited by evaporation, producing a 0.90 cm\textsuperscript{2} active area. A schematic representation of the full device architecture is shown in Figure 5.2.1. The electrical properties of test devices were characterized using a four-probe voltage source/ammeter (Keithley 2425). Current-voltage measurements were taken using a solar simulator (Model 10500, Abet Technologies) running at 1000 Wm\textsuperscript{-2} (1 sun illumination).
5.3 Imaging Characterisation of Graphene Oxide Thin Films

SEM images (Figure 5.3.1) were taken of GO flakes deposited, on a cleaned and plasma-ashed silica substrate via spin coating of GO solution in water. It can be seen that the coverage of GO flakes is not complete across the surface, with up to 25 - 35% of the surface remaining uncovered. This is due to the hydrophobic nature of the silica substrate, which repels the aqueous GO solution, as demonstrated by contact angle measurements given in the appendices (Figure 10.4.1). However, for imaging purposes this gives the opportunity to examine single GO flakes at the edges of the main GO film. From the SEM images, it is possible to see flakes on the surface of approximately 500 nm in diameter. The images show a wide range of flake shapes and sizes but give no quantifiable information about the thickness of the flakes present. The surface coverage percentage and average flake sizes are however only an estimate, determined from the SEM images using a particle analysis method in the image processing program ImageJ.
After optimisation, GO was deposited onto ITO substrates and imaged using SEM (Figure 5.3.2). The SEM images show complete coverage of the GO across the surface. The image in (b) shows a flake with a diameter of approximately 1 µm which is similar to flakes seen in Figure 5.3.1. SEM images of GO on both ITO and silica are difficult to image as flakes often generate a static charge under the SEM beam. This is a strong indication that the conductivity of the GO flakes is very low. While SEM imaging allows for rough estimates of flake sizes, it provides no information about either flake or film thicknesses.

AFM profiles of the GO films are presented in Figure 5.3.3. The height of the flake shown in Figure 5.3.3 (Parts A-C) was determined by AFM to be 1.07 nm which is characteristic of a mono-layer flake of GO as suggested in literature, given the presence of oxygen functional
groups above and below the graphene surface. AFM imaging also gives information on the roughness of the GO film, with a RMS roughness of 0.65 nm, which is considered a very smooth surface. A smooth surface is important as it allows for close contact between the GO film and the active layer, maximising surface area and subsequently efficiency of the hole transporting layer. The optimised deposited GO film thickness was then measured, by carefully scratching the thin GO layer off the surface of the ITO slide and measuring the difference in height from the ITO surface to the top of the GO film (Figure 5.3.3). The film thickness of the GO shown in D, was determined to be 2-3 nm.

![Image](image_url)

**FIGURE 5.3.3** AFM (IMAGE AREA = 5 X 5 µm², Z-SCALE = 20 nm) IMAGE OF A GO FILM ON AN ITO SURFACE (A) AND 3D REPRESENTATION (B). (C) SHOWS THE HEIGHT PROFILE FOR THE LINE SECTION IN (A) USED TO MEASURE THE HEIGHT OF SINGLE GRAPHENE OXIDE FLAKE. (D) SHOWS A SCRATCHED GO FILM ON AN ITO SURFACE, USED TO MEASURE THE THICKNESS OF A GO FILM.

### 5.4 Graphene Oxide Interfacial Layers in Organic Photovoltaics

OPV devices were fabricated according to the methodology detailed in Section 5.2, and used to test the potential of GO as a HTL. This required the selection of the optimal spin speed and concentration of solution to ensure a good film coverage and the best layer thickness. Literature examples using P3HT:PC₆₀BM devices demonstrate that the ideal GO HTL
thickness is approximately 1 nm, representing a monolayer thick film covering 100% of the surface, produces an optimal OPV performance.\textsuperscript{103} Starting with different concentrations of GO and using a constant spin speed of approximately 2000 rpm, initial test devices were fabricated and are detailed in Table 5.4-1.

<table>
<thead>
<tr>
<th>Concentration</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>No HTL</td>
<td>0.45</td>
<td>11.11</td>
<td>51.51</td>
<td>2.58</td>
</tr>
<tr>
<td>GO 0.5 mg/mL</td>
<td>0.54</td>
<td>9.25</td>
<td>41.10</td>
<td>2.05</td>
</tr>
<tr>
<td>GO 2 mg/mL</td>
<td>0.57</td>
<td>10.13</td>
<td>53.94</td>
<td>3.11</td>
</tr>
<tr>
<td>GO 5 mg/mL</td>
<td>0.75</td>
<td>4.22</td>
<td>27.39</td>
<td>0.87</td>
</tr>
<tr>
<td>PEDOT:PSS standard</td>
<td>0.88</td>
<td>11.71</td>
<td>55.94</td>
<td>5.76</td>
</tr>
</tbody>
</table>

It is possible to see the potential for improvement based on the initial device characteristics. While no single device in the series reaches the performance capabilities of the PEDOT:PSS reference device, there is room for improvement. It can be assumed that GO 0.5 mg/mL deposits the lowest quantity of GO onto the surface. This is reflected by the $V_{oc}$ value of 0.54V, which is only slightly higher than the device with no HTL of 0.45V. Conversely, the device using 5 mg/mL concentration is assumed to deposit the most GO material and therefore ensuring the highest surface coverage. This high surface coverage results in a $V_{oc}$ of 0.75V. However, the increased thickness of the film is detrimental to the optical properties of the layer, blocking incoming light and therefore lowering the $J_{sc}$ and FF. The highest performing GO device was made using 2 mg/mL, which had a $V_{oc}$ value of 0.57V, which suggests a complete coverage was lacking. Therefore, 2 mg/mL was used as a set concentration and the spin speed was adjusted to ensure a more complete coverage was achieved. The characteristics of these devices were included in Table 5.4-2.

<table>
<thead>
<tr>
<th>Spin Speed</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>GO 1000 rpm</td>
<td>0.78</td>
<td>11.35</td>
<td>46.64</td>
<td>4.13</td>
</tr>
<tr>
<td>GO 1500 rpm†</td>
<td>0.70</td>
<td>11.26</td>
<td>42.09</td>
<td>3.32</td>
</tr>
<tr>
<td>GO 2000 rpm</td>
<td>0.59</td>
<td>8.20</td>
<td>45.50</td>
<td>2.20</td>
</tr>
<tr>
<td>GO 3000 rpm</td>
<td>0.58</td>
<td>8.57</td>
<td>45.78</td>
<td>2.27</td>
</tr>
<tr>
<td>PEDOT:PSS Standard</td>
<td>0.80</td>
<td>11.60</td>
<td>46.24</td>
<td>4.26</td>
</tr>
</tbody>
</table>

† GO 1500rpm device used an alternative ETL, using TiO$_x$ instead of BCP.
The highest performance characteristics were observed for devices spin coated at approximately 1000 rpm. Fast spin speeds caused a drop in $V_{oc}$, which suggests that faster spin speeds cause a drop in surface coverage, producing areas where no HTL is present. The devices with 2 mg/mL GO spun at 1000 rpm show similar characteristics to the PEDOT:PSS reference standard, implying further improvements would be possible through utilisation of optimised active layer devices.

Therefore, GO was incorporated into optimised PCDTBT:PC$_{70}$BM test devices with both TiO$_x$ and BCP as an ETL. These devices were also compared with the standard HTL material PEDOT:PSS, and with a “no HTL” device as a reference. The J-V data for these devices is shown in Figure 5.4.1 with the average device characteristics presented in Table 5.4-3. The J-V data primarily shows a difference between devices with HTLs when compared with no HTLs. This is shown by the $V_{oc}$ increasing from 0.46V to 0.82 and 0.88V for GO and PEDOT:PSS respectively, which results in an increase of PCE from approximately 2.6% to >5% for GO. This clearly shows that the addition of GO as a HTL is working favourably compared with no HTL.
FIGURE 5.4.1 JV CURVE FOR PCDTBT:PC$_{70}$BM SOLAR CELLS WITH THE ARCHITECTURE AL|ETL|PCDTBT:PC$_{70}$BM|HTL|ITO|GLASS, WHERE THE HTL IS EITHER NO HTL (BLACK UP-TRIANGLES) PEDOT:PSS (RED DOWN-TRIANGLES) OR GO (BLUE DIAMONDS), AND THE ETL IS EITHER EVAPORATED BCP (TOP) OR SOLUTION PROCESSED TiO$_x$ (BOTTOM).

TABLE 5.4.3 OPTIMISED OPV DEVICE CHARACTERISTICS USING DIFFERENT CHARGE TRANSPORT LAYERS. THE DEVICE ARCHITECTURE UTILISED WAS THE STANDARD AL|ETL|PCDTBT:PC$_{70}$BM|HTL|ITO|GLASS SET UP.

<table>
<thead>
<tr>
<th>ETL</th>
<th>HTL</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BCP</td>
<td>No HTL</td>
<td>0.45</td>
<td>11.11</td>
<td>51.51</td>
<td>2.58</td>
</tr>
<tr>
<td></td>
<td>PEDOT:PSS</td>
<td>0.88</td>
<td>11.74</td>
<td>58.66</td>
<td>6.04</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>0.81</td>
<td>11.48</td>
<td>53.65</td>
<td>5.01</td>
</tr>
<tr>
<td>TiO$_x$</td>
<td>No HTL</td>
<td>0.46</td>
<td>11.57</td>
<td>50.88</td>
<td>2.71</td>
</tr>
<tr>
<td></td>
<td>PEDOT:PSS</td>
<td>0.88</td>
<td>11.25</td>
<td>53.29</td>
<td>5.28</td>
</tr>
<tr>
<td></td>
<td>GO</td>
<td>0.83</td>
<td>11.04</td>
<td>56.03</td>
<td>5.13</td>
</tr>
</tbody>
</table>

When comparing GO based devices with their PEDOT:PSS counterparts, it is again the $V_{oc}$ that shows a reduction of approx. 0.05 V between the GO and PEDOT:PSS devices. The reduction in $V_{oc}$ may be caused by incomplete GO film coverage creating some areas where there is no HTL present and therefore lowering the average $V_{oc}$ across the whole device area. Alternatively, it could be caused by a small mismatch of the band energies, as GO has a work function of 4.6 - 4.9 eV compared to the more favourable PEDOT:PSS which has a work
function of 5.2 eV. The band energy diagrams for both of the GO device architectures used are shown in Figure 5.4.2. This mismatch creates a larger energy difference between the GO work function and the HOMO level of the PCDTBT active layer polymer. The PCDTBT polymer is one of the deepest HOMO level polymers available for solar cell production, and therefore the same reduction in $V_{oc}$ is not expected for P3HT, PTB7 or other active layer polymers. This agrees with the literature which reports similar efficiencies for GO HTLs compared with PEDOT:PSS using other active layers such as P3HT and PTB7.103,107 It should be noted that all devices were fabricated with an active area of 0.64 cm$^2$, which reduces possible masking effects that can produce artificially increased PCEs.161 The active area of 0.64 cm$^2$ selected is approx. 10 times larger than active areas commonly reported,162 and a significant step closer to the goal of 1 cm$^2$, after which it is reported PCE’s remain consistent across larger areas.161,162

![Figure 5.4.2 Band Energy Diagrams for the PCDTBT:PC$_{70}$BM Devices Using GO HTLs Taken from Literature. (Reprinted with permission from Ref 104. Copyright 2014, AIP Publishing LLC.)](image)

The EQE for the test devices presented in Table 5.4-3 are shown in Figure 5.4.3. The GO HTL based devices show similar features to the no HTL device with a maximum at approximately 400 nm and a plateau extending from 440 to 545-580 nm. There is very little difference in EQE intensities between the no HTL and GO based devices with a slight increase only visible when using BCP as an ETL. This is reflected in the small increase in $J_{sc}$ for GO-BCP devices. The lack of difference for TiO$_x$ devices is interesting when compared with the $J_{sc}$ presented in Table 5.4-3, however this is likely due to small variations in the light output of the solar
simulator used to measure $J_{sc}$. By integrating the area under EQE curve, it is possible to confirm the accuracy of the measured $J_{sc}$ value (Table 5.4-4).

![EQE plot for PCDTBT:PC$_{70}$BM solar cells with the architecture AL|ETL|PCDTBT:PC$_{70}$BM (HTL/ITO) Glass, where the HTL is either no HTL (black up-triangles) PEDOT:PSS (red down-triangles) or GO (blue diamonds), and the ETL is either evaporated BCP (top) or solution processed TiO$_x$ (bottom).](image)

**Figure 5.4.3 EQE plot for PCDTBT:PC$_{70}$BM solar cells with the architecture AL|ETL|PCDTBT:PC$_{70}$BM (HTL/ITO) Glass, where the HTL is either no HTL (black up-triangles) PEDOT:PSS (red down-triangles) or GO (blue diamonds), and the ETL is either evaporated BCP (top) or solution processed TiO$_x$ (bottom).**

<table>
<thead>
<tr>
<th>ETL</th>
<th>BCP</th>
<th>TiO$_x$</th>
</tr>
</thead>
<tbody>
<tr>
<td>HTL</td>
<td>No HTL</td>
<td>PEDOT:PSS</td>
</tr>
<tr>
<td>J$_{sc}$ from JV (mA/cm$^2$)</td>
<td>11.11</td>
<td>11.74</td>
</tr>
<tr>
<td>J$_{sc}$ from EQE (mA/cm$^2$)</td>
<td>9.70</td>
<td>10.89</td>
</tr>
</tbody>
</table>

By examining the EQE maxima, there is a clear difference between the GO and no HTL EQE when compared with PEDOT:PSS. Both GO and No HTL devices show EQE maxima between approximately 350 – 425 nm while the EQE maxima for the PEDOT:PSS devices shifts to approximately 450 – 500 nm. The EQE data for both the GO and PEDOT:PSS reach around 70% with the EQE maxima for the no HTL device approaching 65% for BCP and 70% for TiO$_x$. It is interesting to note that PEDOT:PSS has a lower EQE for the 350 – 410 nm range. This is
because the thickness of the PEDOT:PSS film causes a red shift in the EQE spectra, resulting in the higher EQE maxima at approximately 450 – 500 nm. Similar effects have been observed in the literature for photodetectors using different PEDOT:PSS thicknesses.\textsuperscript{163}

To investigate the effect of increasing GO HTL disorder on overall device performance, test devices were fabricated using the GO\textsubscript{MRHxx} series. Devices made with GO\textsubscript{MRH11} and GO\textsubscript{MRH12} resulted visibly rough films resulting in the short circuiting of devices. This is not unexpected, as the XRD results demonstrate that GO flakes in GO\textsubscript{MRH11} and GO\textsubscript{MRH12} are held much closer together and therefore are significantly more difficult to ensure complete exfoliation. The J-V curves for devices with GO\textsubscript{MRH13} and GO\textsubscript{MRH15} HTL’s are presented in Figure 5.4.4 for comparison.

![J-V Curve Graph](image)

**FIGURE 5.4.4 J-V CURVES AND CORRESPONDING DEVICE CHARACTERISTICS FOR STANDARD TEST DEVICES FABRICATED WITH GO\textsubscript{MRH13} AND GO\textsubscript{MRH15} HTLS.**

Similar device efficiencies of 4.19\% are found for both GO\textsubscript{MRH13} and GO\textsubscript{MRH15} HTL devices, however the individual characteristics highlight a few differences. For example, the GO\textsubscript{MRH13} HTL device characteristics show a reduced \(V_{oc}\) of 0.69V compared with a \(V_{oc}\) value of 0.82V for GO\textsubscript{MRH15}. As previously discussed, reductions in \(V_{oc}\) are associated with either incomplete coverage of the HTL, or a mismatch of bands resulting in a lower of the effective band gap. Given the difference in band gap for GO\textsubscript{MRH13} and GO\textsubscript{MRH15} of approximately 1eV as shown by the Tauc plots in Section 3.6, it is reasonable to assume the reduction in oxygen
functionality has resulted in a rising of the $GO_{MRH13}$ work function increasing the possibility of developing a mismatch of bands between the ITO and the active layer. Additionally, the lesser extent of oxidation, caused by limiting the $KMnO_4$ used to synthesize $GO_{MRH13}$, may have lowered the concentration of $GO_{MRH13}$ stable in water, leading to a lower concentration of GO being deposited, and consequently detrimentally affecting the overall film coverage. Both of these suggestions could be used to explain the reduction in $V_{oc}$ for $GO_{MRH13}$ test devices. Comparatively, devices with the $GO_{MRH15}$ HTL layer exhibit a lower FF which could be the result of increases in disorder adversely affecting the transporting properties of the HTL. It is therefore possible that a trade-off is occurring between the effective work function of the material and the disorder present. To bypass this, it is necessary to adjust the work function of the material without adding to the material disorder and affecting the charge transport properties. This idea will be explored further in Section 5.7.

5.5 Graphene Oxide Organic Photovoltaic Lifetime Testing

To test the lifetime of the fabricated devices, GO devices were measured periodically under different atmospheric conditions and compared with PEDOT:PSS devices. The first set of lifetime tests were completed using unencapsulated devices in ambient air conditions (Figure 5.5.1). Over the course of 100 hours, both PEDOT:PSS and GO suffer from serious degradation issues resulting in complete device failure. This is reflected in the loss of $J_{sc}$, FF and PCE for both GO and PEDOT:PSS. It is interesting to note that the $V_{oc}$ for PEDOT:PSS is not reduced, while that for GO is. Currently, the reason for this is not fully understood. It is possible the HTL layer separates away from the active layer, creating preferential pathways through the device. For a 40 nm polymer layer as in the PEDOT:PSS device, this doesn’t create an issue, but for a layer of GO flakes stacked on top of each other 2-3 nm high, this could lead reduction of active layer electrode interface causing $V_{oc}$ degradation. Regardless, the overall PCE degradation is significant, which confirms that both PEDOT:PSS and GO HTL based devices do not perform well in ambient air conditions. This is due to the lack of protection from atmospheric water provided to the active layer. A similar effect is seen for devices with no HTL.
Consequently, a second set of test devices were stored under nitrogen in an inert, dry environment, and only removed from that environment to be measured. Ideally these devices would be measured inside the nitrogen environment however this was not possible with the experimental set up available. This type of lifetime test is considered similar to a shelf life test as the device is not run constantly throughout the experiment. It can also be considered similar to an encapsulated device as the effect of external atmospheric factors have been minimised. The results of this lifetime test is shown in Figure 5.5.2, with the degradation of PCE presented seperately in Figure 5.5.3. Initially, there is a small burn-in period over the first 1,000 hours, followed by a linear degradation period thereafter. This behaviour is seen in the literature and is identified as the expected degradation characteristics of PCDTBT based devices as shown previously (Figure 2.2.14). From Figure 5.5.2, it is clear to see that the devices are much more stable when stored in a nitrogen atmosphere or pseudo-encapsulated. In this case, the devices lasted almost 8,000 hours with only minimal degradation (Table 5.5-1). The $V_{oc}$ remains constant after the initial burn-
in period with only minimal losses, as does the $J_{sc}$. The FF suffers slightly higher losses in the linear degradation period for both GO and PEDOT:PSS devices, with PEDOT:PSS devices suffering higher losses than GO HTL devices. This results in a slightly steeper slope for the PCE degradation, as shown in Figure 5.5.3.

![Graphs showing degradation of OPV device characteristics over time](image)

**Figure 5.5.2** OPV device characteristics for unencapsulated PCDTBT:PC$_{70}$BM devices with PEDOT:PSS (black) and GO (red) HTLS stored under nitrogen between measurements in air taken over the course of 7700 hours.

**Table 5.5-1** Device characteristics for unencapsulated PCDTBT:PC$_{70}$BM devices with different HTLS, measured after initial fabrication (0 hour) and after 7700 hours.

<table>
<thead>
<tr>
<th>HTL</th>
<th>Time (hrs)</th>
<th>$V_{oc}$ (V)</th>
<th>$J_{sc}$ (mA/cm$^2$)</th>
<th>FF (%)</th>
<th>PCE (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PEDOT:PSS</td>
<td>0</td>
<td>0.86</td>
<td>9.47</td>
<td>57.09</td>
<td>4.7</td>
</tr>
<tr>
<td></td>
<td>7700</td>
<td>0.81</td>
<td>9.63</td>
<td>41.25</td>
<td>3.2</td>
</tr>
<tr>
<td>GO</td>
<td>0</td>
<td>0.70</td>
<td>9.60</td>
<td>52.14</td>
<td>3.5</td>
</tr>
<tr>
<td></td>
<td>7700</td>
<td>0.58</td>
<td>9.87</td>
<td>44.78</td>
<td>2.6</td>
</tr>
</tbody>
</table>
To extrapolate the plots and the estimate the lifetime, as shown in Figure 5.5.3, a linear plot is extrapolated after the initial burn in period. The initial burn in period was determined based on drops in $V_{oc}$ in the initial phase as shown in Figure 5.5.2. The time after the burn in period is set to 100% normalised efficiency and labelled $t_{100}$ and the lifetime is determined by the time taken to reach $t_{80}$, or the time when the normalised efficiency reaches 80% with respect to $t_{100}$. This method for extrapolation is detailed in the literature and highlighted previously in Figure 2.2.14. The extrapolation suggests that the PCE at $t_{80}$ for PEDOT:PSS devices is approximately 5100 hours, while for GO the PCE at $t_{80}$ approximation is 8300 hours. This is estimated as a 62% lifetime improvement for GO devices when compared with PEDOT:PSS. It should be noted that the devices are measured in air, and therefore the shelf lifetime may be longer with sufficient encapsulation. Furthermore, as shown in Figure 5.5.1, GO degrades faster than PEDOT:PSS when exposed to the atmosphere, and therefore may show additional shelf lifetime improvements in a completely encapsulated system.

A possible cause for this improvement in lifetime can be seen when looking at the series resistance of the devices (Figure 5.5.4). An increased series resistance decreases FF, which
subsequently decreases PCE. An increase in series resistance is characteristic of degradation of the bulk materials, limiting charge transport through the device. One of the causes of this reported in the literature is the diffusion of indium and tin from the ITO layer into the active layer. This diffusion process is expedited through the use of PEDOT:PSS, likely because of its acidic properties. Furthermore, the effect PEDOT:PSS has on series resistance is accelerated under humid conditions, as shown in the literature, which is consistent with acidic etching of the ITO layer. Therefore, it is proposed that the acidic nature of PEDOT:PSS causes the increase in series resistance when left in storage conditions, possibly through the acidic etching and subsequent diffusion of indium and tin ions. Consequently and to conclude, it is favourable to use GO when compared with PEDOT:PSS for HTLs in OPV as this acidic degradation does not occur. However, GO HTL devices still require encapsulation to restrict the ingress of water and oxygen into the device.

![Graph showing series resistances for unencapsulated PCDTBT:PC70BM devices with PEDOT:PSS (black) and GO (red) HTLS stored under nitrogen between measurements in air taken over the course of 7700 hours.](image)

**FIGURE 5.5.4** SERIES RESISTANCES FOR UNENCAPSULATED PCDTBT:PC$_{70}$BM DEVICES WITH PEDOT:PSS (BLACK) AND GO (RED) HTLS STORED UNDER NITROGEN BETWEEN MEASUREMENTS IN AIR TAKEN OVER THE COURSE OF 7700 HOURS.

### 5.6 Graphene Oxide Organic Photovoltaic Conduction Mechanisms

In order to investigate the conduction mechanisms occurring in the functional devices, the unilluminated current-voltage data was examined with respect to common electrical conduction mechanisms. This allows for an estimation of the charge transport limiting
mechanism across the device as a whole. Changes in this approximation with different HTL’s would indicate that the HTL plays a role in limiting the conduction throughout the device. To determine the limiting mechanism, four charge transport mechanisms were investigated; two bulk limiting (SCLC and PF) and two electrode limiting (Schottky and FN), as previously detailed in Section 2.2.2. The devices used for analysis utilised the TiO$_x$ electron transport layer, with the device architecture of Al/TiO$_x$/PCDTBT:PCBM/HTL/ITO as in Section 5.4.

The plot for the SCLC conduction mechanism is shown in Figure 5.6.1. All of the graphs show the presence of 2 distinct regions, labelled in Table 5.6-1 as V < 0.5 and V > 0.5 respectively. All 3 plots show a current voltage relationship of $J \propto V$ in the V < 0.5 region, which is attributed to the Ohmic region of SCLC, where Ohm’s law is dominant. In the second V > 0.5 region, the current voltage relationship rises to $J \propto V^7$ for PEDOT:PSS and GO devices, and $J \propto V^9$ for devices with no HTL. This is attributed to the trap filling region detailed previously (Section 2.2.3), which has a relationship of $J \propto V^{l+1}$ where l describes the distribution of trap levels, which suggests the presence of trap states in the device as a whole. This is not unexpected and agrees with similar devices reported in literature.$^{83}$

![Figure 5.6.1 I-V Data Fitted into Conduction Mechanism Plots for Space Charge Limiting Current (SCLC) Conduction Mechanism, for OPV Devices with the Architecture Al/TiO$_x$/PCDTBT:PCBM/HTL/ITO, Where the HTL is Either (A) No HTL, (B) PEDOT:PSS or (C) GO. (D) Replots the Data for All the Devices on the Same Axis for Comparison.](image-url)
**TABLE 5.6.1 SCLC CHARACTERISTICS FOR OPV DEVICES WITH VARYING HTLS**

<table>
<thead>
<tr>
<th>HTL Configuration</th>
<th>( V &lt; 0.5 )</th>
<th>( V &gt; 0.5 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>No HTL</td>
<td>( J \propto V )</td>
<td>( J \propto V^7 )</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>( J \propto V )</td>
<td>( J \propto V^7 )</td>
</tr>
<tr>
<td>GO</td>
<td>( J \propto V )</td>
<td>( J \propto V^7 )</td>
</tr>
</tbody>
</table>

Charge transport using a PF mechanism can be described using the following equation, as discussed in Section 2.2.2,

\[
J \propto E \exp \left( - \left( \frac{\phi_w - e\beta_{PF}E^2}{kT} \right)^{1/2} \right) \quad \text{where } \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{1/2} \quad \text{Equation 38}
\]

As shown in the derivations in the appendix (Section 10.5), this equation can be rearranged into a \( y = mx + c \) linear regression form. By plotting \( \ln(J/E) \) against \( E^{0.5} \) and extrapolating the linear portion of the graph which is present at high fields, it is possible to determine the estimated barrier height (\( \phi_w \)) and the relative permittivity (\( \varepsilon_r \)) for the device to compare with expected values. As previously discussed, the PF effect requires a high electric field to be observed, and therefore the low field regions are discounted from the extrapolation. Figure 5.6.2 shows the PF model fitted data, with the extrapolations used, shown as dashed lines, while Table 5.6-1 shows the calculated values of \( \phi_w \) and \( \varepsilon_r \).
The values of the barrier heights ($\phi_w$) estimated according to the PF model show a decrease of barrier height with addition of a HTL, which would be expected. This would suggest that the barrier is present at the interface between the ITO and the active layer. With a work function of 4.70 eV for ITO, and 5.50 eV for the HOMO level of the PCDTBT polymer, a value of approximately 0.80 eV for the No HTL device would be an accurate estimate for this transition. Furthermore, the work function value of 4.85 eV suggested for GO in the literature would also lead to a barrier height of approximately 0.65 eV between the GO layer and the HOMO level of the PCDTBT polymer. However, the relative permittivities ($\varepsilon_r$) estimated for the devices using the PF model are too low to be reasonable, with expected values ranging from approximately 3 - 12 for most polymer materials. It can therefore be concluded that the PF effect is not the dominant conduction limiting mechanism.

Similar to the PF effect, the Schottky effect can be described by the following equation,
\[ J \propto T^2 \exp \left( -\frac{\phi_w - e \beta_{Sch} E^2}{kT} \right) \text{ where } \beta_{Sch} = \left( \frac{e}{4\pi \epsilon_0 \epsilon_r} \right)^{\frac{1}{2}} \quad \text{Equation 39} \]

Therefore, by plotting \( \ln(J/T^2) \) against \( E^{0.5} \) and extrapolating the linear section of the fit at high fields, it is possible to estimate the barrier height \( \phi_w \) and the relative permittivity \( \epsilon_r \) as with the PF model. Figure 5.6.3 shows the model fits for the Schottky effect, with the estimated values of \( \phi_w \) and \( \epsilon_r \) provided in Table 5.6-3. The values estimated for the barrier heights are similar to the PF effect, which as previously discussed agrees with the expected values based on the barrier between the ITO and the HOMO level of the active layer. Furthermore, there is a difference between GO and PEDOT:PSS of 0.04 eV which could translate to the difference between the V\(_{oc}\) of the functional devices. It is suggested that this is caused by the lower work function of PEDOT:PSS compared with GO and is therefore expected. This suggests a Schottky dependence may be occurring. However, the relative permittivities estimated using the Schottky model are again too low to be reasonable, suggesting that Schottky is not the dominant charge limiting conduction mechanism.
Fowler Nordheim tunnelling is possible due to the ultra-thin nature of the layers in use. As detailed in Section 2.2.3, it is possible to estimate the barrier height ($\phi_w$) by plotting the $\ln(J/E^2)$ against $1/E$ and extrapolating the linear region of the graph present at high fields to give the tunnelling probability ($\kappa$) which can be used to estimate the barrier height. The plots used for extrapolation are presented in Figure 5.6.4. The barrier heights presented in Table 5.6-4, range from $1.54 \times 10^{-6}$ - $1.83 \times 10^{-6}$ eV, which are too low to be reasonable. Therefore, it is safe to assume that FN tunnelling is not the conduction limiting mechanism.
In conclusion, the conduction mechanism fits suggest that the conduction limiting mechanism is most likely to be SCLC, as expected values are not observed in the other mechanisms. This would fit with previously studied devices in the literature. Estimations for the barrier height based on both the PF and Schottky model suggest that the presence of either PEDOT:PSS or GO reduces the size of the barrier present. Furthermore, the Schottky fits suggest that the barrier height reduction can be linked to the $V_{oc}$ of the functional devices, and therefore the alignment of bands using transport layers is important to maximise device performance. It also suggests that the difference between the GO and PEDOT:PSS devices presented in Section 5.3, could be improved by closer alignment of the bands without the addition of extra resistance caused by material disorder. However, it is important to recognise that the electrical conduction mechanisms are primarily used for...
single material systems, and therefore may only be used as rough estimation tools when dealing with the complexity of full OPV device architectures.

5.7 Iron - Reduced Graphene Oxide Interfacial Layer in Organic Photovoltaic

It was postulated that the presence of iron oxide in the shell of the iron nanoparticle could result in a shift in work function for Fe-rGO which would subsequently provide better matching for OPV applications. This was confirmed through the use of Kelvin probe microscopy, in which Fe-rGO was determined to have a work function 0.3 eV lower than standard GO. This gives Fe-rGO an effective work function between 4.9 – 5.2 eV, which is similar to the work function range of PEDOT:PSS. The exact work function measured by Kelvin probe can vary in response to a number of factors, including the underlying substrate choice especially in ultra-thin films.\(^{166}\)

Regardless, it was proposed that the lower work function for Fe-rGO could result in an OPV device performance matching that of PEDOT:PSS. Therefore, Fe-rGO thin films were deposited via spin coating (2000 rpm, 1 minute) from IPA solution (1.5 mg/mL) and OPV test devices were fabricated as detailed previously. IPA was found to disperse Fe-rGO only temporarily and therefore it was essential to spin coat the Fe-rGO – IPA solutions immediately after sonication using the probe sonicator. The device characteristics for a Fe-rGO OPV device is shown in Figure 5.7.1 and compared to devices with either PEDOT:PSS, GO or no HTL.

![Figure 5.7.1 JV Curve for PCDTBT:PC\(_{70}\)BM Solar Cells with the Architecture AL|TiO\(_2\)|PCDTBT:PC\(_{70}\)BM|HTL|ITO|Glass, Where the HTL is Either No HTL (Black Up-Triangles) PEDOT:PSS (Red Down-Triangles) or GO (Blue Diamonds) or Fe-rGO (Green Squares). The Characteristics for the Fe-rGO HTL Device Are Shown.](image-url)
The $V_{oc}$ of 0.88V for the Fe-rGO device suggests an improvement of band alignment caused by the Fe-rGO material, which is consistent with the work function estimates made through kelvin probe microscopy. The $V_{oc}$ also reaches the same limit as devices made with a PEDOT:PSS HTL, which is considered the maximum $V_{oc}$ associated with the PCDTBT:PC$_{70}$BM system, based on the expected HOMO and LUMO levels. Therefore, it can be assumed that the $V_{oc}$ for the device is no longer limited by charge transport in the HTL layer, but limited by the active layer materials. This improvement results in a device PCE of 5.7% which is comparable with devices fabricated using PEDOT:PSS.

The EQE spectra for the Fe-rGO device is shown in Figure 5.7.2. Similar to GO devices, the Fe-rGO device shows an increased absorption in the 350 – 425 nm region, when compared with PEDOT:PSS device which exhibits a higher absorption in the 400 – 600 nm region. However, unlike the GO device, the Fe-rGO device displays higher absorption in this region as well, with an EQE maximum at approximately 460 nm. This is expected due to the increase in thickness of the Fe-rGO layer compared to the GO, which is required to incorporate the iron nanoparticles without greatly increasing the surface roughness.

![Figure 5.7.2 EQE Plot for Fe-rGO (Green) and PEDOT:PSS (Red) HTL Based PCDTBT:PC$_{70}$BM Solar Cells with the Standard Architecture of Al|TiO$_{2}$|PCDTBT:PC$_{70}$BM|HTL|ITO|Glass.](image)

In conclusion, the increase in device performance when using Fe-rGO compared to GO demonstrates the potential of the material for this form of application. However, the unfavourable dispersion properties cannot be overstated. Irreversible aggregation of Fe-rGO
severely limits its potential for use in thin film applications such as OPV devices. However, with the ever advancing push into methods of producing stable graphene solutions, it is possible that these avenues may be utilised to produce stable solutions of Fe-rGO in the future.

5.8 SUMMARY

In this chapter, GO thin films were deposited via spin coating for use in OPV devices. Through the optimisation of solution concentration and spin speeds, an optimal thickness was established and tested as a HTL in high efficiency PCDTBT:PC\textsubscript{70}BM test devices. GO HTL device efficiencies of approximately 5% closer to PEDOT:PSS reference device efficiencies, but with a small drop in \(V_{oc}\) which lowers the overall device performance.

With efficiencies close to PEDOT:PSS devices established, the lifetime of un-encapsulated GO HTL based devices were compared to PEDOT:PSS devices. In air, it was shown that both suffer from limited stability, caused by the ingress of water into the active layer. However, GO HTL devices demonstrate enhanced shelf lifetimes when isolated from the external atmosphere leading to a 62% increase in shelf lifetime compared to PEDOT:PSS devices. This leads to the conclusion that GO is more intrinsically stable than PEDOT:PSS in the device. The instability of PEDOT:PSS in devices results in a rise in series resistance not seen for the GO based devices, and it is theorised this degradation is caused by the acidity of PEDOT:PSS resulting in etching of the ITO layer. It can therefore be concluded that GO can be used to improve the shelf lifetime of OPV devices and possibly the operating lifetime of fully encapsulated devices.

The drop in \(V_{oc}\) seen in GO HTL devices is exaggerated through using GO materials with less oxygen functionality, as shown by using examples from the GO\textsubscript{MRhxx} series. It is proposed that this drop in \(V_{oc}\) is the result of work function differences resulting in increased barrier heights as suggested by the conduction mechanism plots. To counteract this, Fe-rGO is used as an HTL owing to its lower work function when compared with GO. This results in the fabrication of devices with \(V_{oc}\) values as high as PEDOT:PSS and, additionally, the maximum theoretical \(V_{oc}\) for the PCDTBT:PC\textsubscript{70}BM system. However, deposition of the Fe-rGO material is not easy, limiting its effectiveness as a solution processed alternative to either PEDOT:PSS or GO.
6 Graphene Oxide Material Interfaces for Thin Film Applications

6.1 Introduction
In this chapter, rGO_{VC} thin films are produced via a spray coating method. rGO_{VC} is selected based on figures of merit established in Chapter 4 which suggest that rGO_{VC} produces the least disordered rGO variant material of the methods examined. The film production and subsequent thin film characterisation are detailed in Section 6.2. In Section 6.3, the electrical resistance across these rGO_{VC} thin films is reported as the vitamin C reduction process occurs. Section 6.4 compares the optical properties of the rGO_{VC} films, showing the effect of using a heated substrate has on deposition control. Finally, Section 6.5 discusses some of the advantages and disadvantages of the use of rGO_{VC} thin films for transparent conducting electrodes compared with the industrial standard ITO. The overall goal of this chapter is to determine how effective rGO thin films can be as a cheap alternative to ITO, and how limitations to rGO thin films can be overcome.

6.2 Production and Characterisation of Reduced Graphene Oxide Thin Films
rGO_{VC} films were produced via the spray coating of a GO / vitamin C solution. Spray coating was undertaken using a RS Pro Air Brush connected to a nitrogen gas line pressured at 15 PSI. Initial attempts at spraying rGO_{VC} in solution were hindered by the agglomeration of rGO materials in most solvents. A selection of solvents were chosen based on favourable Hansen solubility parameters and claims made in literature. However, these all proved unsuccessful at dispersing rGO_{VC} for a significant period of time (Figure 6.2.1). This is likely to be due to the loose definition of rGO materials in literature which, as shown in Chapter 4, can vary greatly in physical properties. Therefore, it was determined that a method for reducing GO on the substrate surface was required, thus allowing GO or partially reduced GO to remain dispersed in water during the spray coating process. To investigate the plausibility of this method, an excess of vitamin C (50 mg) was added to a solution of GO (10 mL, 1 mg/mL IPA: water 50:50 mixture) and either sprayed immediately as prepared (t_0), or left to react for 1 (t_1) or 2 (t_2) days to encourage a small degree of reduction prior to spray coating. IPA was added to improve the wetting properties on the surface and to ensure rapid drying at room temperature, which limits the formation of droplets on the surface. Poor wetting properties and the subsequent formation of droplets on the surface lead to a non-uniform film being fabricated.
Raman analysis of the deposited rGO\textsubscript{VC} films (t\textsubscript{0}, t\textsubscript{1} and t\textsubscript{2}) are shown in Figure 6.2.2. An increase in the I\textsubscript{D}/I\textsubscript{G} ratio, from 0.79 to 1.39, and a decrease in FWHM\textsubscript{D}, from 105 cm\textsuperscript{-1} to 47 cm\textsuperscript{-1} is seen on progressing from t\textsubscript{0} to t\textsubscript{2}, both of which demonstrate a decrease in disorder as seen in the reduction of GO (Section 4.3). It is interesting to note that the high I\textsubscript{D}/I\textsubscript{G} ratio and low FWHM\textsubscript{D} suggest that the disorder is lower for rGO\textsubscript{VC} reduced in IPA: water mixture compared to rGO\textsubscript{VC} reduced solely in water (Section 4.3). It is possible that the rGO\textsubscript{VC} produced in water becomes insoluble in the water as the reduction progresses and consequently agglomerates effectively cutting off the reduction process. In the case of an IPA: water mixture, it is possible that as the reduction progresses, the rGO flakes are solvated by the IPA, lessening hydrophobic aggregation and allowing further reduction by the vitamin C. Additionally, the Raman analysis shows the increase of the D’ peak at 1615 cm\textsuperscript{-1} as a result of an increased number of sp\textsuperscript{2} chains, resulting in a significant shoulder to the G peak in the Raman spectra for t\textsubscript{2} and signalling a progression in reduction.
To summarise, despite the unfavourable solubility properties of rGO\(_{\text{VC}}\) in a variety of solvents, it is possible to spray coat a film of GO, or partially reduced GO (as the Raman suggests for \(t_1\) and \(t_2\)), with vitamin C present which may allow for reduction to occur on the surface of the substrate.

### 6.3 Conductivity Testing of Reduced Graphene Oxide Thin Films

This section investigates the effect of surface reduction on the conductivity of thin rGO films, for both vitamin C and thermal reduction methods. Vitamin C was added to GO solutions and subsequently spray coated, as discussed in Section 6.2. For this section, rGO thin films were deposited onto IPA washed glass slides (75mm x 25mm) before contacts were applied at each end using metallic silver paint. As a reference, \(t_{\text{ref}}\) was prepared which contained no vitamin C solution, and therefore solely demonstrated the contribution of the thermal reduction of GO. The spray coated films were then heated to 250°C and allowed to cool back to room temperature to ensure the reduction had taken place. The electrical resistance of the thin films were measured in real time throughout the heating and cooling profile. The measured resistance is then plotted against the temperature as shown in Figure 6.3.1.
As can be seen, $t_{\text{ref}}$ shows a progressive decrease in resistance as the temperature increases, with a greater decrease at approximately 200°C, reaching a value of 3.28 MΩ for GO with no Vitamin C. This rapid decrease in resistance can be compared with the TGA results (Section 4.4) which show significant mass losses at approximately 200°C, attributed to the loss of oxygen functional groups from the GO flakes. During the cooling of $t_{\text{ref}}$ the bulk resistance rises slightly from 3.28 MΩ to 21.55 MΩ at room temperature. This increase in resistance with decreasing temperature demonstrates that GO / rGO materials have a negative temperature coefficient which is consistent with results presented in the literature. The starting resistances for $t_{\text{ref}}$, $t_0$ and $t_1$ are all in the $10^{12}$ Ω range, while $t_2$ has a starting resistance in the $10^{10}$ Ω range. This shows that the reduction is occurring regardless of the increase in temperature associated with the heating profile. Upon the addition of the vitamin C, in $t_0$, $t_1$ and $t_2$, the temperature at which the reduction occurs lowers from 200°C to approximately 100°C. It is interesting to note, that $t_0$ also reduces at approximately 100°C even though it has not been given significant time to reduce in solution. This shows that the reduction is progressing, in part, on the surface of the substrate.
This is reflected in the Raman analysis of the thin films which were measured before and after heating up to 100, 200 and 250 °C separately. The values for the $I_D/I_G$ ratio and FWHM$_D$ are plotted in Figure 6.3.2 while the individual Raman spectra are presented in the appendices (Section 10.6). The Raman analysis of $t_{\text{ref}}$ shows little to no change over the 250 °C range which is consistent with the Raman analysis of rGO$_{TA}$ also presented in Section 4.3. However, for $t_0$ and $t_1$, there is an increase in $I_D/I_G$ ratio up to approximately 1.3 and a decrease in FWHM$_D$ to fewer than 60 cm$^{-1}$ when the samples are heated to 100 °C, reaching similar values as those for the $t_2$ thin film. This shows that upon heating to 100 °C, the reduction on the surface of the substrate occurs to the same degree as if it were left to reduce in solution. It is interesting to note that $t_2$ does not change further upon heating to 100 °C which implies that $t_2$ has already reached the end point of the current reaction in solution prior to spray coating. Given the lack of change in disorder parameters for $t_2$ below 150 °C, it can be assumed that the resistance in $t_2$ is not limited by the disorder present on individual flakes. This suggests that the disorder present on rGO flakes, as measured by Raman spectroscopy, is not limiting the conductivity of rGO thin film networks.

Furthermore, after the temperature reaches 250 °C, the $I_D/I_G$ ratio for $t_0$, $t_1$ and $t_2$ drops significantly to values similar to that for rGO$_{TA}$. A similar effect is seen in the FWHM$_D$ values which increase significantly. This indicates that at higher temperatures, such as 250 °C, the reduction via vitamin C begins to degrade the quality of the rGO material produced creating more defects. This is confirmed by examining the TGA profile for the GO when mixed with vitamin C ($t_0$) (Figure 6.3.3). The TGA profile for the $t_0$ film shows that the majority of mass loss happens between 150 and 300 °C, before the thermal decomposition at approximately
400 - 475°C. This thermal decomposition temperature is lower when compared with rGO$_{VC}$ prepared from solution at 80 °C, which confirms that the vitamin C degrades the material at temperatures above 150°C as shown in the Raman results. Given that it is reported that Vitamin C decomposes at approximately 190°C, releasing molecular weight equivalents to a CO$_2$ and a H$_2$O molecule,$^{169}$ it is possible that the breakdown of the vitamin C into gaseous by-products causes defects to form on the neighbouring GO flakes. This could be caused by an increase in internal stress as gas bubbles form and attempt to escape the film. It is also possible that the proposed furfural ring that remains after vitamin C decomposition could interact with the GO/rGO flakes at the elevated temperature. The exact mechanism remains unclear and would require further research to understand completely.

![Figure 6.3.3 TGA Profile for rGO$_{VC}$ Thin Film ($T_0$) After Deposition Via Spray Coating Without Drying at Elevated Temperature. The Derivative Weight Loss is Shown in Red.](image)

The degradation of the GO flakes after 150°C is important when considered in parallel with the resistance measurements in Figure 6.3.1 which shows no increase in bulk resistance between 150 and 250°C where the material degradation occurs. This implies that the resistance of the thin film is no longer limited by the quality of the material present after the initial reduction. This will be further discussed in Section 6.4. To understand the effect that the concentration of vitamin C has on the reduction process, the vitamin C concentration was varied prior to immediate deposition ($t_0$), (Figure 6.3.4). A similar rapid drop in resistance is seen between 80 – 125°C, which corresponds to the reduction process. For a 1:1 GO: vitamin C ratio, this is followed by a small shoulder also visible on the derivative
curve profile, from approximately 125 - 175°C. Taking into consideration the rapid decrease in resistance caused by thermal annealing at 180°C, it is not unreasonable to assume that this second shoulder is caused by thermal reduction, which causes additional reduction after the initial vitamin C has been depleted. This is assumed because of the lack of this shoulder in subsequent experiments, where higher concentrations of vitamin C allow for more reduction than is possible with thermal annealing.

**FIGURE 6.3.4 (TOP) RESISTANCE OF rGO\textsubscript{VC} PLOTTED AS A FUNCTION OF TEMPERATURE FOR DIFFERING CONCENTRATIONS OF GO: VITAMIN C. (BOTTOM) THE CHANGE IN RESISTANCE IN rGO\textsubscript{VC} WITH RESPECT TO TEMPERATURE. THE INSET SHOWS THE ONSET TEMPERATURE OF REDUCTION FOR DIFFERENT GO: VITAMIN C RATIOS.**

By taking the first and second derivative of the electrical resistance vs temperature profile, it is possible to determine the reduction onset temperature as shown in the inset of Figure 6.3.4. This shows that the lowest reduction temperature is seen for a 1:3 GO: Vitamin C ratio, reaching a temperature as low as 85°C, which is an acceptable temperature for a wide range of plastic substrate materials, including for example, Polyethylene terephthalate (PET). Increasing the concentration of vitamin C further increases the reduction onset temperature, which could suggest that a thicker layer of vitamin C is being formed around the GO flakes, causing some heat insulation effects, which delay heat transfer and create a thickness dependent difference between the measured temperature and the temperature
of the GO flakes in the film. To further probe the effect of temperature on the thin film reduction, GO\textsubscript{VC} (1:5 GO: Vitamin C ratio) films were reduced at different temperatures (Figure 6.3.5).

![Graph showing resistance of rGO\textsubscript{VC} films plotted as a function of time at varying reduction temperatures. Dashed lines represent extrapolated values based on the established trend.](image)

**FIGURE 6.3.5** RESISTANCE OF rGO\textsubscript{VC} FILMS PLOTTED AS A FUNCTION OF TIME AT VARYING REDUCTION TEMPERATURES. DASHED LINES REPRESENT EXTRAPOLATED VALUES BASED ON THE ESTABLISHED TREND.

This investigation demonstrates that at lower temperatures, the reduction is occurring; however the rate of reduction has been slowed significantly. Given that vitamin C is capable of reducing GO to some extent at room temperature over a much longer period of time, this is not surprising. It is however, further proof that reduction is occurring on the substrate surface.

In summary, a method of producing conductive rGO\textsubscript{VC} films via spray coating is detailed, which bypasses the need for the dispersion of rGO in solvents. The vitamin C is shown to reduce GO on the surface of the substrate, which reduces the need for a stable exfoliated rGO solution. Additionally, the effect of temperature on the reduction process is shown, with real time measurements showing a significant drop in resistance at approximately 80-125°C corresponding to the complete reduction of GO via vitamin C. Analysis of the Raman
data shows that heating further increases the quantity of disorder in the films, without adversely affecting the resistance of the as a whole.

6.4 Optical Properties of Vitamin C Reduced Graphene Oxide Thin Films

The two requirements for transparent conducting electrodes are high optical transparency and high electrical conductivity across the surface, which equates to a low sheet resistance. The optical properties of rGO\textsubscript{VC} films were measured using UV-Vis spectroscopy, for a series of different spray volumes, and thus different expected film thicknesses. Spray volumes of 5, 10 and 15 mL (1 mg/mL GO solution and 5 mg/mL Vitamin C in 50:50 IPA: water) were deposited onto glass substrates and measured before and after reduction at 150°C (Figure 6.4.1).

![Figure 6.4.1 Optical Transmission of GO (Dashed Lines) and rGO\textsubscript{VC} (Solid Lines) Spray Coated onto a Cold Glass Substrate.](image)

The glass slide substrate is shown to have 90.9% transmittance (measured at 550 nm). With the glass slide, rGO\textsubscript{VC} films prior to reduction display a transmittance of 88.0%, 80.5% and 83.0% for 5, 10 and 15 mL, respectively. After reduction, the values for the rGO\textsubscript{VC} films on glass drop to 78.3%, 58.0% and 60.4% respectively. This is consistent with UV-Vis data presented in Chapter 4, which showed an increased absorption across the spectra, but a reduction in the optical absorption in the UV region (< 300 nm), when compared with GO. The increased GO optical absorption in the UV is not observable in this set of data, as the glass substrate dominates absorption in this region.
The optical properties show an increase in optical absorption with increased spray volume, for the unreduced GO films up to 10 mL, with the film deposited using 15 mL of solution showing no further increase in optical absorption. This is also the case after reduction, which suggests that a deposition limit has been reached before the 10 mL deposition. It is likely that, due to the relatively low volatility of the water solvating the GO flakes, additional GO solution simply washes additional flakes off the still wet surface. Therefore, in the interest of controlling the thickness, the substrate was heated to 150°C, both to ensure reduction of GO flakes on contact with the surface, and to speed up the drying process, so that additional control of the thickness could be established via varying the spray volume. The UV-Vis spectra for rGO\textsubscript{VC} films deposited onto heated substrates are provided in Figure 6.4.2.

Upon a heated substrate, the thickness of the film and therefore the transmission of light through the film can be directly related to the volume of GO solution sprayed. This shows that heating the substrate during deposition not only removes the deposition limit associated with spraying on a wet substrate, but also ensures more of the GO remains on the substrate. This can further be seen by comparing the transmission using the film deposited using 5 mL of solution for both heated and non-heated substrate, (67.4% and 78.3% respectively, measured at 550 nm) which shows an increase in optical absorption for the heated substrate, indicating a higher quantity of GO flakes adhering to the surface and thus a thicker film. The presence of a tangible relationship between spray volume and

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**FIGURE 6.4.2** OPTICAL TRANSMISSION OF rGO\textsubscript{VC} SPRAY COATED ONTO A HEATED (150°C) GLASS SUBSTRATE. (A) SHOWS THE TOTAL OPTICAL TRANSMISSION THROUGH THE FILM AND THE GLASS, WHILE (B) SHOWS THE OPTICAL TRANSMISSION AT 550 nm PLOTTED AGAINST THE VOLUME OF GO\textsubscript{VC} SPRAYED.
optical transmission when depositing on a heated substrate demonstrates the increase in control provided by heating the substrate during the deposition process.

6.5 **Vitamin C Reduced Graphene Oxide Transparent Conducting Electrodes**

To be competitive as a transparent conducting electrode, the material is required to exhibit similar sheet resistance and transparency as ITO. Commercial ITO can be bought with a sheet resistance of 10 Ω\(\square\)\(^{-1}\) and a transparency of 83% in the visible light region (390-700nm). This equates to a \(\sigma_{DC}/\sigma_{Op}\) value of approximately 30 (Section 2.2.2). The sheet resistance of rGO\(_{VC}\) films, deposited on a hot substrate, (Section 6.3) were measured using the technique known as transmission line measurement (TLM) (Figure 6.5.1).

As expected, an increase in spray volume results in a decrease in sheet resistance. It can be assumed that this is because the thickness of the film increases as demonstrated by the increased UV-Vis absorption (Section 6.4.) Therefore, it is important to take the thickness of the film into account when comparing the sheet resistance with the optical transmission values (Figure 6.5.2). As previously discussed in Section 2.2.2, the figure of merit \(\sigma_{DC}/\sigma_{Op}\) is a useful measure of transparent conducting electrodes, as it is independent of thickness. The \(\sigma_{DC}/\sigma_{Op}\) for the differing spray volumes is included in Figure 6.5.2. The comparison of resistance to optical absorption shows an exponential relationship, with the very high

![Figure 6.5.1 Transmission Line Measurements of rGO\(_{VC}\) Films with Differing Spray Volumes Sprayed onto a Heated (150°C) Substrate. The Calculated Sheet Resistance for Each Film is Shown on the Graph.](image-url)
optical transmission samples showing exponentially higher resistance. Similarly, at increased optical absorptions the change in resistance is much less significant. $\sigma_{DC}/\sigma_{Op}$ increased with increasing spray volume. It is proposed that this is because the $\sigma_{DC}$ value is based on the assumption of a complete film, and therefore doesn’t take into account reductions in resistance due to incomplete surface coverage. Therefore, an increase in spray volume would lead to increased surface area, resulting in a higher $\sigma_{DC}/\sigma_{Op}$.

Regardless, the highest conductivity ratio, $\sigma_{DC}/\sigma_{Op}$, is shown to be 0.046, which is not high enough to compete with the likes of ITO at a value of 30. It is comparable with some other deposited rGO thin films. However, the Raman analysis in Figure 6.3.2 suggests that the quantity of disorder is increasing after thermal annealing above 150°C, potentially caused as a consequence the breakdown of vitamin C, and yet the resistance is shown not to rise with this increase in disorder. This suggests that the conductivity along individual flakes, which is determined by $sp^2$ content and therefore disorder, is not limiting the resistance across the film as a whole.

This can be explained by considering the two dimensional nature of conductivity through a graphite based material. In the basal plane of graphite (the ‘a’ and ‘b’ directions) conductivity is high due to the low band gap between the conduction and valance bands. However, through the plane, the crossing of the (3.35 Å) interlayer spacing represents a large barrier to conduction, resulting in the insulating nature of graphite in the ‘c’ direction. Values of $2.5 – 5.0 \times 10^{-6}$ and $3000 \times 10^{-6}$ Ω.m are often quoted in literature for the resistivity

**FIGURE 6.5.2 (A) SHEET RESISTANCE VS OPTICAL TRANSMISSION COMPARISON, (B) THE CONDUCTIVITY RATIO, $\sigma_{DC}/\sigma_{Op}$ COMPARED WITH VOLUME OF rGO SPRAYED ON A HEATED (150°C) SUBSTRATE.**
of graphite in the ‘ab’ and ‘c’ directions respectively. Every flake to flake junction requires travel in the c direction, resulting in a significant increase in resistance. It is therefore proposed that the resistance can be decreased further by increasing the size of sheets, thus lowering the number of junctions required to create a percolating network.

Furthermore, this theory suggests that by decreasing the interlayer distance, a further decrease in resistance could be achieved. This could be used to help explain why literature sources report increased conductivity of rGO films with increased pressure. The application of pressure could lead to a distance reduction in the c axis, resulting in decreased junction resistances, and the subsequent increase in conductivity observed. Finally, the theory suggests that to improve the conductivity of rGO based percolating networks, some form of interconnect is required with the aim of effectively bridging flakes, and thus lowering the junction resistances.

6.6 SUMMARY

In summary, a new low temperature method of producing rGO films was demonstrated through the simultaneous spray coating of GO and vitamin C. It was demonstrated that vitamin C is capable of reducing GO on the surface of a substrate, which bypasses one of the major challenges of working with rGO and graphene like materials; the successful simultaneous solubilisation, dispersion and exfoliation of the material. Using real time temperature and electrical resistance monitoring, it is possible to track the conductivity of the rGO film through the course of the reduction. The reduction of GO using vitamin C shows a sharp decrease in resistance between 80 - 125°C, depending on the ratio of vitamin C to GO, which coincidences with significant decreases in disorder as shown in the Raman spectra.

However, Raman spectroscopy on the partially reduced t₂ rGO_{VC} film suggests that rGO flake disorder is not the primary limiting factor when it comes to overall film conductivity. This is confirmed by the lack of change to resistance measured after the rGO_{VC} film is heated to 250°C, which indicates that the disorder has increased, likely due to the thermal decomposition of residual vitamin C. This is consistent with literature sources that argue that flake based undoped graphene networks are limited to a conductivity ratio of approximately 0.7, and therefore incapable of competing with traditional transparent
conducting electrodes such as ITO with a conductivity ratio of 30. The results presented in this chapter support this conclusion, although the improvement of flake to flake junctions and larger flake sizes are possible methods for increasing the conductivity ratio.
7 GRAPHENE OXIDE MATERIALS FOR ENVIRONMENTAL MEMBRANES

7.1 INTRODUCTION
In this chapter, the adsorption properties of GO materials are investigated through the use of the fluorescent dye molecule Rhodamine B (RhB). Initially, the GO_{MHRxx} series is used to establish the optimum state of oxidation for GO adsorbent materials (Section 7.2). To compare with GO powder materials, the synthesis of rGO based porous sponges is optimised in Section 7.3. In Section 7.4, Raman spectroscopy is used to examine the rGO sponges and conclusions are drawn regarding the effect of residual vitamin C on the surface during heat treatment. The rGO sponges are imaged using SEM techniques to confirm the presence of pores capable of adsorbing the dye (Section 7.5). This is supplemented with an X-ray Micro CT study, where the rGO sponges are used to adsorb metallic silver particles, which act as a contrast agent, allowing for accurate 3D reconstructions of the sponge’s internal structure to be established. With the porous nature of the sponge imaged, Sections 7.6 compares the adsorption capabilities of the rGO sponges in comparison to the GO_{MHRxx} series given in Section 7.2. Finally, Section 7.7 demonstrates the advantages associated with the use of magnetic rGO in adsorbent applications. The overall aim of this chapter is to determine to what extent GO/rGO materials can be used to make more effective adsorbent materials.

7.2 ADSORPTION OF RHODAMINE B USING GRAPHENE OXIDE
In this section, UV-Vis spectroscopy is used to determine the concentration of RhB dye adsorbed after the addition of GO from the GO_{MHRxx} series, in order to determine the most effective adsorbent GO material for RhB. The principle UV-Visible absorption maxima (\(\lambda_{\text{max}}\)) for RhB dye (Figure 7.2.1) is the peak present at 554 nm. According to the Beer-Lambert Law, the intensity of light absorbance is directly proportional to the concentration of the analyte. Therefore, it is possible to plot a calibration curve to estimate the concentration of RhB ([RhB]) based on the absorbance at \(\lambda_{\text{max}}\).
Using Beer-Lambert Law, in conjunction with the calibration curve produced for Rhodamine B absorption (inset, Figure 7.2.1), it is possible to determine the molar absorption coefficient for Rhodamine B dye in water. The slope of the calibration curve for [RhB] from 0 mg/L to 10 mg/L is 107,903 with an adjusted $r^2$ value of 0.999 indicating that the fit is good. Therefore, the molar attenuation coefficient for Rhodamine B in aqueous solution is $107,903 \text{ L.mol}^{-1}\text{cm}^{-1}$. This is consistent with values presented in literature.  

In order to determine the optimum GO based material to adsorb RhB dye, 10 mg from each of the GO$_{MRHxx}$ series was added to a solution of RhB dissolved in water (150 μg, 10 ml of 15 mg/L). The quantity of the RhB dye adsorbed per gram of adsorbent ($q_t$) over the course of 300 minutes for GO$_{MRH11}$ – GO$_{MRH14}$ is shown in Figure 7.2.2. It shows GO$_{MRH11}$ adsorbs only a very small percentage of the dye, with approximately 2.5% of the total dye adsorbed after 300 minutes. This is contrasted with GO$_{MRH12}$ which demonstrates a higher adsorption of approximately 25% of the total dye adsorbed after 300 minutes, which is higher than the activated carbon from a commercially available water filter (10 mg of activated carbon...
taken from a Brita Fill&Go water filter disc). However, this is low in comparison to $\text{GO}_{\text{MRH13}}$ and $\text{GO}_{\text{MRH14}}$ which show almost complete adsorption after less than 1 hour. This greatly increased adsorption is proposed to be the result of the increased interlayer distance, as shown by XRD (Section 3.5), which allows for adsorption between the GO sheets for $\text{GO}_{\text{MRH13}}$ – $\text{GO}_{\text{MRH16}}$. This can be seen by examining the intraparticle diffusion plots for $\text{GO}_{\text{MRH11}}$ and $\text{GO}_{\text{MRH12}}$ (Figure 7.2.2). As discussed in Section 2.2.4, by plotting the amount of dye adsorbed at time $t$ ($q_t$) against $t^{0.5}$, it is possible to estimate whether the process of intraparticle diffusion dominates. $\text{GO}_{\text{MRH11}}$ and $\text{GO}_{\text{MRH12}}$ both show intercepts close to 0, which indicate that both are limited by the ingress of dye molecules through the intraparticle diffusion process, which fits with the proposed understanding of the adsorption process. The small interlayer distance for $\text{GO}_{\text{MRH11}}$ and $\text{GO}_{\text{MRH12}}$ restricts water ingress between the layers, as shown by FTIR spectroscopy (Section 3.7), which provides further evidence that interlayer adsorption is unlikely to occur.

To examine the adsorption capacity of $\text{GO}_{\text{MRH13}}$ – $\text{GO}_{\text{MRH16}}$, a larger quantity of RhB was dissolved in water at the same concentration (1.5 mg in 100 mL or 15 mg/L) and the kinetics were analysed according to pseudo first order and pseudo second order rate kinetics as detailed in Section 2.2.5. In brief, $\log(C)$ is plotted against time for pseudo first order, while $t/q_t$ is plotted against time for pseudo second order and the expected linear relationships are compared using $r^2$ values (Figure 7.2.3). The pseudo first order model does not produce
a linear relationship, with $r^2$ values ranging from 0.35 – 0.73. However, the pseudo second order model produces a linear relationship for the adsorption process, resulting in $r^2$ values of 0.999 or better. Therefore, it can be assumed that the adsorption of RhB onto GO follows the pseudo second order kinetic model, and therefore the adsorption capacities and rate constants can be calculated (Table 7.2-1).

![Graph](image)

**FIGURE 7.2.3** (A) RhB concentration plotted against time, in which a linear relationship is expected for the pseudo first order kinetic model and (B) $t/q_t$ plotted against time, in which a linear relationship demonstrates pseudo second order rate kinetics.

**TABLE 7.2-1** Pseudo second order rate constants ($k''$) and equilibrium constants ($q_e$) for GO$_{MRH13}$ – GO$_{MRH16}$

<table>
<thead>
<tr>
<th>GO$_{MRHxx}$</th>
<th>GO$_{MRH13}$</th>
<th>GO$_{MRH14}$</th>
<th>GO$_{MRH15}$</th>
<th>GO$_{MRH16}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$k''$</td>
<td>0.00057</td>
<td>0.00367</td>
<td>0.00221</td>
<td>0.00350</td>
</tr>
<tr>
<td>$q_e$ (mg/g)</td>
<td>94.3</td>
<td>106.5</td>
<td>112.6</td>
<td>105.6</td>
</tr>
</tbody>
</table>

As evidenced by the higher pseudo second order rate constants, GO$_{MRH14}$, GO$_{MRH15}$ and GO$_{MRH16}$ show increased adsorption rates when compared with GO$_{MRH13}$, which suggests that additional oxidation increases the rate of RhB adsorption. Unfortunately, this results in
a trade off, as the most oxidised samples are also more likely to remain in solution making recovery difficult. This is demonstrated through the adsorption of a small quantity of dye (150 μg, 10 ml of 15 mg/L) over 3120 minutes (52 hours), followed by examination of the concentration of GO still present in solution after 52 hours (Figure 7.2.4). The concentration of GO present was determined by measuring the absorption at 700 nm, at which RhB does not optically absorb, and comparing it to a series of GO_{MRHxx} solutions of known concentrations. This is compared with the amount of dye adsorbed at equilibrium (q_e) which is directly related to the number of active sites available for adsorption. Additionally, RhB exhibits a shift in peak maxima from 554 nm to approximately 575 - 590 nm when adsorbed onto GO_{MRH15} and GO_{MRH16} as shown in Figure 7.2.4. This indicates the presence of π stacking between GO and the RhB dye, and therefore shows that a fraction of the GO complexes with RhB and remains in the solution.\textsuperscript{175} GO remaining stable in solution, either as GO or through complexation as GO-RhB, is unfavourable for adsorbent applications, as it leads to further contamination of the solution, which is undesirable. Consequently, this needs to be taken into consideration when comparing adsorbing materials.

![Figure 7.2.4](image)

**FIGURE 7.2.4** (A) UV-ABSORPTION SPECTRA OF THE GO_{MRHxx} SERIES AFTER ADSORPTION OF RhB DYE FOR 52 HOURS, AND (B) THE GO CONCENTRATION LEFT IN SOLUTION AFTER 52 HOURS, AND THE AMOUNT OF DYE ADSORBED AT EQUILIBRIUM (q_e). THE ARROW IN (A) SHOWS A SHIFT IN PEAK MAXIMA FOR GO_{MRH15} AND GO_{MRH16} THE GREEN REGION IN (B) SHOWS GO_{MRH13} AND GO_{MRH14} WHICH BOTH EXHIBIT A HIGH ADSORPTION CAPACITY AND A LOW GO CONCENTRATION REMAINING IN SOLUTION.

From this analysis, it is clear that the most effective adsorbing material from the GO_{MRHxx} series is GO_{MRH13}, as it shows increased adsorption capacity when compared with GO_{MRH11} and GO_{MRH12}, and also does not remain in solution after adsorption as is the case for GO_{MRH15} and GO_{MRH16}, and to a lesser extent GO_{MRH14}. It is therefore suggested that the
effective adsorption of RhB onto GO materials has two elements to it. The first is the increase of interlayer distance as shown by XRD, effectively opening up the surface area by allowing diffusion of dye molecules into the layers of the GO material. This greatly increases the surface area and therefore number of active sites available for adsorption. However, the second element is that a good GO adsorbing material must not show long term solution stability after adsorbing, to avoid further contamination of the solution with GO/GO-RhB complexes. Unfortunately, these two factors are often linked, with GO materials with larger interlayer distances exhibiting better solubility properties as a result of an increase in oxygen functionality between the GO layers. While rGO materials have shown a decreased interlayer distance, as shown in Section 4.5, and subsequently a reduced $q_e$, it is possible to create porous rGO hydrogel sponges, which could be used to overcome this complication.

7.3 Synthesis of Reduced Graphene Oxide Sponges

rGO sponges were synthesised using methods similar to those detailed in the literature. In brief, GO powder, synthesised via the Hummers’ method detailed in Chapter 3, was dispersed via probe sonication in water at various concentrations. A set concentration of vitamin C was added and dispersed via sonication (Ultrawave Qi 200) for 1 minute to ensure the vitamin C was completely dissolved. This solution was transferred into a reaction vessel (glass vial / plastic tube / beaker), and heated to 80°C for a set period of time. It is noted that sponges can be formed in various shapes depending on the dimensions of the reaction vessel. The starting concentration of both vitamin C and GO were varied, alongside the amount of sonication and the length of time the solution was heated, to examine the optimal conditions for sponge formation. Starting GO solutions of different concentrations are shown before and after sponge formation in Figure 7.3.1. To ensure an excess of vitamin C, a concentration of 15 mg/mL was used in initial investigations with concentrations ranging from 1 – 10 mg/mL, GO solutions showed evidence of sponge formation. However, sponges formed at lower concentrations of GO formed distorted shaped sponges, while the 10 mg/mL solution produced a clearly defined cylindrical sponge similar in shape to the vial reaction vessel. Therefore, for further experiments, 10 mg/mL solutions of GO were used to allow for sponges to be formed with desired shapes conforming to the reaction vessel used.
To establish the minimum amount of vitamin C required to ensure sponge formation, a series of sponges were synthesised using different concentrations of Vitamin C (Figure 7.3.2). It was determined that a concentration of 5 mg/mL of Vitamin C was required to synthesis an rGO sponge using the starting GO concentration of 10 mg/mL, corresponding to a GO: Vitamin C ratio of 2:1. Going below this ratio resulted in reduction of GO to aggregated rGO but did not result in the formation of rGO sponges. Similarly, it was determined that a heating time of at least 1 hour, and an initial sonication time of 1 minute using the probe sonicator was required in order to aid sponge formation. Using the less powerful bath sonicator proved ineffective in dispersing the GO solution to the required level for sponge formation.

To synthesise the Fe-rGO sponges discussed in Section 7.6, vitamin C (60 mg) was added to GO (40 mg) in water (4mL, giving a 10 mg/mL GO solution) and heated to 80°C for 2 hours.
Upon synthesis of the rGO sponge, the iron nanoparticles were added via the addition of the iron resin, as detailed in Section 4.2. In brief, citric acid (0.75 g) is dissolved in water (5 mL), followed by the addition of iron (III) nitrate nonahydrate (1 g). Ethylene glycol (7.5 mL) is then added and the resulting mixture is heated to 80°C while stirring. Upon reaching 80°C, the mixture is placed in a bath sonicator for 30 minutes. This process of heating to 80°C and then sonicating is repeated 3 times. To impregnate the sponge (10 mg), the remaining vitamin C - water solution was decanted and replaced by 2 mL of the iron resin. The iron impregnated sponge was heated to 800°C for 2 hours in a nitrogen filled tube furnace (Carbolite STF 15/180). To create the rGO sponges with silver, used for CT scanning, a similar method was used, replacing the iron resin with a silver based resin. To synthesise the silver resin, citric acid (0.75 g) is dissolved in water (5 mL), followed by the addition of silver nitrate (200 mg). Ethylene glycol (7.5 mL) is added and the same heat and sonication treatment is applied as for the iron resin. The remaining water is decanted as before and replaced by 2 mL of the silver resin. However, instead of heating these rGO sponges with silver nanoparticles as previously, they were instead freeze dried. The silver nitrate in the resin is theorised to react with residual vitamin C on the surface of the sponge to form visible silver particles, and therefore a heating step was not required. To produce contrast between samples in the CT scanning of the silver - rGO sponges, the concentration of the silver resin was adjusted by diluting using additional water. Finally, to establish a within-sample contrast reference for CT imaging, 200 µL of the undiluted silver resin was carefully added to a 10 mg rGO sponge so as to only cover one side of the sponge. The CT analysis of this sponge can be found in the appendix (Section 10.7).

7.4 Raman Analysis of Reduced Graphene Oxide Sponges
To examine the effect of sponge assembly on the GO/rGO material, the sponges were measured using Raman spectroscopy. Raman analysis of the pristine rGO$_{VC}$ sponges is shown in Figure 7.4.1 with peak characteristics of the D and G peaks presented in Table 7.4-1. This supplemented with the Raman analysis of the same sponge after thermal annealing at 300°C, in order to evaluate the thermal stability of the sponge. The sponge maintained its structural integrity with heating, however a difference can be seen in the Raman spectra.
FIGURE 7.4.1 RAMAN SPECTRA FOR rGOVC SPONGES (A) BEFORE AND (B) AFTER A THERMAL ANNEALING AT 300°C.

<table>
<thead>
<tr>
<th>rGOvc Sponge</th>
<th>D Peak</th>
<th>G Peak</th>
<th>Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Peak Position (cm⁻¹)</td>
<td>FWHM (cm⁻¹)</td>
<td>Peak Position (cm⁻¹)</td>
</tr>
<tr>
<td>No TA</td>
<td>1350 ± 3</td>
<td>81 ± 1</td>
<td>1582 ± 5</td>
</tr>
<tr>
<td>TA @ 300°C</td>
<td>1352 ± 2</td>
<td>114 ± 8</td>
<td>1577 ± 3</td>
</tr>
</tbody>
</table>

The main differences seen in the Raman spectra are the significant increase in widths of the D and G peak and the reduction of the I_d/I_g ratio. As discussed in Chapter 3 and 4, for materials like GO and rGO this is characteristic of an increase in disorder, causing a decrease in size of sp² clusters and increase in stress applied to these clusters. The reduction in I_d/I_g ratio from 0.95 ± 0.06 to 0.54 ± 0.06 represents a decrease in cluster size from 1.30 nm to 0.95 nm according to the I_d/I_g ∝ L⁻² relationship for materials like rGO, as demonstrated in Section 4.3. This, coupled with the high FWHM_D and FWHM_G of 114 ± 8 cm⁻¹ and 113 ± 11 cm⁻¹, indicate an increase in disorder caused by thermal annealing at 300°C. This is consistent with results presented in Chapter 6, which showed an increase in disorder for rGOvc thin films with thermal annealing over 200°C when Vitamin C was left on the surface. It is therefore theorised that the vitamin C remains on the surface of the sponge after the
solvent has been driven off, and then causes disorder in the rGO structure as the vitamin C breaks down in a similar fashion as seen in Chapter 6.

When comparing the Raman characteristics of the rGO sponges with those presented for rGO_{VC} films in Chapter 6, similarity can be seen for the D peak (both in width and position) between the rGO_{VC} sponge and the rGO_{VC} thin film left in solution for 24 hours prior to spray coating (t_{1}). As t_{1} was considered an intermediate between the starting GO with vitamin C (t_{0}) and the fully reduced rGO_{VC} (t_{2} and/or rGO_{VC} powder from Chapter 4), it can be concluded that the rGO_{VC} sponge does not reduce to the same level as the rGO films. It is possible that the reduction is limited by the sponge formation effectively blocking possible reduction sites. Alternatively it could simply be that the concentration of vitamin C is enough to form the sponge but not to fully reduce the GO.

However, when comparing the characteristics of the G peak with the trends detailed in Chapter 4, the rGO_{VC} sponges, both pristine and annealed, show a significant increase in peak width, and a significant decrease in the G peak position. This suggests a possible emergence of a peak with a slightly lower peak position compared to the G peak probably caused by some element of the 3D structure of the rGO sponges. There is currently not enough evidence to draw a definitive conclusion on this matter.

In conclusion, the Raman analysis of the rGO_{VC} sponges indicates a partial reduction of GO is achieved in the sponge formation process. It also suggests that thermal annealing of the sponge in the presence of vitamin C results in an increase in disorder similar to that presented for the rGO_{VC} films in Chapter 6.

### 7.5 Imaging of Reduced Graphene Oxide Sponges

To further investigate the porous nature of the rGO_{VC} sponges, SEM and micro-CT images were taken of the rGO_{VC} sponges. For the sponges to survive the vacuum conditions required for SEM imaging, the sponges must be adequately dried. The as-synthesised sponges contain a large amount of water which must be removed to also give an accurate representation of the weight of the sponge. However, removing this water causes the sponge to shrink, as the surface tension of the water is strong enough to cause the sponge to compact. This is demonstrated in Figure 7.5.1 where an rGO_{VC} sponges (10 mg) (A) are taken out of solution (B) then dried either via low temperature (40\(^{\circ}\)C) vacuum drying (C), or
by freeze drying (D). A significant size reduction can be seen when comparing the rGO_{VC} sponge vacuum dried (C) to the sponges in (B) and (D). Both (C) and (D) were weighed and found to be approximately 10 mg.

![Digital photographs of an rGO_{VC} sponge (10 mg)](image)

**FIGURE 7.5.1** DIGITAL PHOTOGRAPHS OF AN rGO_{VC} SPONGE (10 mg) (A) AS SYNTHESISED, (B) AFTER SOLUTION DECANTATION, AND FINALLY AFTER BEING DRIED, EITHER BY (C) LOW TEMPERATURE (40°C) VACUUM DRYING, OR BY (D) FREEZE DRYING. THE SCALE BAR IN (D) REPRESENTS 5mm.

To further investigate the effects of the drying process, SEM images were taken of the sponges. SEM images of the rGO_{VC} sponges were taken using a FEI Quanta electron microscope operating in low vacuum mode (10 – 130 Pa). SEM images of an rGO_{VC} sponge dried by low temperature (40°C) vacuum drying are presented in Figure 7.5.2. The SEM image in (A) shows a cross section of the sponge which highlights a large crater-like hole in the centre of the sponge measuring approximately 1 mm in diameter, as well as a series of smaller holes of approximately 100 - 200 µm in diameter. The holes are shaped randomly and show no signs of uniformity. By zooming in on the edge of the sponge, it is possible to gauge the structure of the outer wall of the sponge. This is shown in (B) and further enlarged in (C). Both (B) and (C) show the rough outer surface of the sponge, which results in a larger surface area than a smooth surface. However, the images do not show whether the outer surface contains holes or micro-pores to the sponge inwards which would increase the surface area dramatically. To investigate this, a sponge was sliced open and an image was taken of the cross section inside the outer sponge surface which is shown in (d). This image shows that micro pores run throughout the sponge, suggesting that the rGO_{VC} sponge is porous and that the surface area of the sponge is not restricted to the outer sponge surface. The SEM image in (D) also shows the effect of the drying process, as large areas of sponge material have densified into more compact, and therefore smoother, regions. This reduces the porosity of the material and therefore reduces the surface area onto which adsorbates can be adsorbed. This is, therefore, obviously detrimental for water purification applications.
By freeze drying the sponge, the surface tension of the water is removed as the water is solidified and subsequently sublimed. This results in less shrinkage in the sponge samples and therefore more effectively maintains the sponge structure. Comparative SEM images for a freeze dried rGO\textsubscript{VC} sponge are presented in Figure 7.5.3. The SEM image in (A) shows a fragment of an rGO\textsubscript{VC} sponge after it has been freeze dried as the fully freeze dried rGO\textsubscript{VC} sponge was too large to image using the SEM equipment. Similar to the low temperature vacuum dried sponge, the freeze dried rGO\textsubscript{VC} sponge has a visibly porous structure with holes of varying sizes. Images (B) and (C) show the edge of the sponge surface with a very rough porous surface. Image (D) shows the top surface of the sponge, which resembles aggregated flakes of graphite. This is likely caused by incomplete exfoliation of the starting graphite oxide, caused by the high 10 mg/mL GO concentration. Image (E) shows a hole of approximately 100 µm diameter within the rGO\textsubscript{VC} sponge structure. Unlike in the low temperature vacuum dried sponge, (F) shows no signs of densification, and a very porous structure visible even at high magnifications. The pores shown in (F) have diameters as small
as 5 - 20 µm. This high porosity should allow for increased adsorption of adsorbates, and therefore is more promising for water purification applications.

CT scanning was selected as a novel method for investigating the sorption of materials into these sponge materials. For this to be successful, a high atomic number element is added to the sponge in order to absorb X-rays and create contrast in the CT scan. Silver was selected for introduction into the sponge because of its well-known antibacterial properties, useful for water filtration applications. Figure 7.5.4 shows SEM images of a sponge fragment which was left to soak in the silver resin described in Section 7.3. Silver particles are clearly visible covering the surface of the sponge in images (A), (B) and (C). By magnifying a flat section of spongy material (D) it is possible to see a selection of silver particles adhered to the surface of the flakes, with sizes ranging from 50 – 500 nm.
FIGURE 7.5.4 SEM IMAGES OF AN rGO\textsubscript{VC} SPONGE FRAGMENT LEFT TO SOAK IN SILVER RESIN BEFORE FREEZE DRYING. SCALE BARS REPRESENT 50 µm (A), 20 µm (B), 5 µm (C), and 2 µm (D) RESPECTIVELY.

With the presence of silver containing particles adsorbed onto the surface confirmed, X-ray CT scanning was used to image rGO\textsubscript{VC} sponges subjected to differing concentrations of the silver resin (0.2, 2 and 20 mg/mL). Micro CT images were taken using an Oxford Instruments XTF 5000 X-ray source with a Molybdenum anode, a Hamamatsu C7942 flat panel detector and a CsI scintillator. Samples were placed on a Micos VT-80 and DT-80 translation and rotation stages with a Corvus-eco controller, and rotated 1° per projection for 360 projections. Each projection is then subsequently composed of 20 individual frames. Initial 2D X-ray projections are shown in Figure 7.5.5 and compared with a digital photograph of the same rGO\textsubscript{VC} sponges. Both the sponges subjected to 2 mg/mL and 20 mg/mL silver resin
solution are clearly visible in the X-ray image, with the 20 mg/mL sponge having high contrast with the background. This shows that the concentration of silver absorbed into the sponge is high enough to efficiently absorb the incoming X-ray photons. Similarly, but to a lesser extent, the 2 mg/mL sample absorbs the incident X-rays producing a notable image. In comparison, a very faint outline can be seen of both the reference and the 0.2 mg/mL samples. This is caused by the small fraction of x-ray photons being absorbed by the carbon sponge itself. However the returned signal is not significant enough to provide any further details about the structure of the sponge. The image contrast with the background becomes more visible by taking a line profile of the X-ray projection, transecting all the sponges as shown in Figure 7.5.6.

![Figure 7.5.5 X-ray projection (top) and digital photograph (bottom) of 4 rGO\textsubscript{w} sponges left to soak in silver resin of differing concentrations before freeze drying. (From left to right, 0 mg/mL reference, 0.2 mg/mL, 2 mg/mL and 20 mg/mL respectively.)](image)
From the X-ray projections, it is possible to extrapolate a series of slices, which can be translated into a 3D representation of the sponge structure. An example of these slices and the corresponding 3D models are presented (Figure 7.5.7) for two different concentrations of silver resin (2 mg/mL and 20 mg/mL) added to an rGO\textsubscript{VC} sponge. From the cross section shown in (C), it can be observed that there is a large amount of silver containing particles built up on the edge of the sponge. The model also shows the presence of a large void in the centre of the sponge. Initially, it was unclear whether this was a region of sponge that was not coated in silver, or whether it was a void in the sponge. However, it was subsequently shown to be a void after the sponge was broken into smaller pieces. It is difficult to judge how far into the sponge the silver has absorbed in (C). It could be argued that there are signs that the silver has reached the edges of the void, as there is a slight increase in intensity around the edges of the void. However it is not conclusive when taking line profiles across the cross section as shown in Figure 7.5.8. Complete absorption of silver throughout the sponge is much clearer when using the higher concentration of silver resin (D – F).

Furthermore, the presence of higher intensity regions around the edges of the void indicates that the silver resin has filled the sponge prior to adsorption. The increased intensity around the edges of some of the voids suggests that the silver resin is able to fill the void, leading to aggregation of the resin to the nearest surface over the course of time.
similar to the external surface. The aggregation of the silver containing particles on the external surface is visible in the synthesis process and results in a grey colouration of rGO_{VC} sponges dipped into the silver resin. This is expected as the vitamin C reduces silver nitrate to silver metal nanoparticles which easily aggregate together to form silver containing aggregates. The surface rendering in (E) shows the increased intensity around the voids in the 20 mg/mL silver resin rGO_{VC} sponge. From the presence of the silver coating on the edge of the void, it can be inferred that the void was filled upon addition of the silver resin and is therefore the edges surrounding the void are porous to some degree.

FIGURE 7.5.7 3D MODELS GENERATED FROM MICRO CT X-RAY PROJECTIONS OF rGO_{VC} SPONGES LEFT TO SOAK IN SILVER RESIN OF 2 mg/mL (A – C) AND 20 mg/mL (D - F). FOR EACH SET A 3D MODEL IS CONSTRUCTED FROM THE CT DATA (A + D), SURFACES ARE RENDERED AND SMOOTHED USING THE HIGHEST INTENSITIES (B + E) AND A CROSS SECTION IS TAKEN (C + F). EACH VOXEL REPRESENTS 50 µm³.
FIGURE 7.5.8 LINE PROFILES TRANSECTING CROSS SECTIONS OF rGO_{VC} SPONGES LEFT TO SOAK IN SILVER RESIN OF 2 mg/ml (A) AND 20 mg/ml (B). THE RED BOXES SHOW AGGREGATIONS OF SILVER AT EDGES, WHILE THE BLUE BOXES REPRESENT VOIDS IN THE SPONGE. THE INSETS SHOW THE EXAMINED CROSS SECTION SLICE AND THE POSITION OF THE LINE PROFILE. EACH PIXEL OF THE CROSS SECTION REPRESENTS 50 µm².

The absence of carbon material inside the voids of the sponge suggests the presence of a gas pocket in the sponge during synthesis. Owing to the hydrophobic nature of the rGO\textsubscript{VC} flakes, it is possible that the sponge forms around bubbles present in the solution to minimise the rGO\textsubscript{VC} flakes interaction with water. This would allow for potential tuning of the porous nature of the sponges, through manipulation of microbubbles as sponge nucleation sites. It is also possible that the reduction process produces gases (such as carbon monoxide/ carbon dioxide) therefore forming bubbles in situ, which act as a nucleation site for the sponge as previously described. The thermal reduction of GO is shown to release carbon oxide gases as a by-product of the reduction at temperatures above 150°C,\textsuperscript{57} however given the results presented in Chapter 6 where the presence of vitamin C lowers the reduction temperature. Vitamin C could also lower the temperature at which these by-products are released. This would explain the presence of such large voids in sponges formed in solutions that have been degassed somewhat through sonication.

In conclusion, SEM images of the sponges showcase their porous nature, with a wide range of pore sizes present. The method of drying the sponge is shown to make a significant difference on the closure of these pores, and the subsequent densification of the sponges. Through the addition of silver nitrate, which reacts with residual vitamin C on the surface of the sponge to form silver containing particles, it is possible to examine the 3D structure of the sponge using micro CT scanning. The micro CT images confirm the presence of pores throughout the sponge, leading to adsorption of the silver particles throughout the sponge’s
structure. The CT images also highlight the presence of voids within the sponges, which suggest gas pockets are present during the synthesis process. Whether these gas pockets are essential to the synthesis or a resultant part of the synthesis is unclear. However, it is clear that the rGOVC sponges are capable of adsorption throughout the sponge volume, as demonstrated through the use of micro CT and silver containing particles.

7.6 Adsorption of Rhodamine B using Reduced Graphene Oxide Sponges
To compare the adsorption properties of the rGOVC sponges with GO materials presented in Section 7.2, RhB adsorption tests were conducted for the rGOVC sponge. Figure 7.6.1 shows SEM images of the rGO sponge after it has been placed in Rhodamine B (RhB) solution. The SEM images in (a) and (b) show the outer surface of the sponge is coated with RhB. The RhB forms distinctive spikey crystallites on the sponge surface as shown in (c) and (d). The sponges can therefore be used to adsorb RhB dye from solution where the reduction of the dye solution concentration can be quantified using UV-Visible spectroscopy. The porosity and available surface area of the sponges will ultimately determine how much of the RhB dye can be adsorbed.

**FIGURE 7.6.1 SEM IMAGES OF AN rGOVC SPONGE AFTER BEING LEFT TO SOAK IN RhB. SCALE BARS 200 μm (A), 50 μm (B), 10 μm (C) AND 5 μm (D).**
To compare the adsorption properties of rGO\textsubscript{VC} sponges with the adsorption properties of the GO\textsubscript{MRHxx} series presented in Section 7.2, a 10 mg rGO\textsubscript{VC} sponge was added to a solution of RhB dissolved in water (10 ml of 15 mg/L) and the quantity of dye adsorbed measured as before (Figure 7.6.2). Initially, the uptake of dye into the sponge is slow, with approximately 20% of the dye adsorbed over the course of 300 minutes. This is comparable with GO\textsubscript{MRH11} and GO\textsubscript{MRH12}, which is unsurprising as the interlayer distance of rGO\textsubscript{VC} was measured as 3.63Å using XRD (Chapter 4), which is similar to GO\textsubscript{MRH11} and GO\textsubscript{MRH12} and significantly smaller than the rest of the series. It is interesting to note that as time progresses, the amount of dye adsorbed begins to increase. This suggests that the adsorption of the dye is initially limited by the first stage of the sorption process which, as previously discussed in Section 2.2.5, involves the transfer of the dye molecules from the liquid phase into the adsorbent material. For the GO powder samples, this process is negated by the dispersion of the GO into the liquid phase with the dye molecules. For the rGO\textsubscript{VC} sponges, dye molecule must diffuse into the sponge prior to intraparticle diffusion along the pore walls of the sponge and finally adsorption.

![Figure 7.6.2](image_url)

**FIGURE 7.6.2** RhB ADSORBED BY GO/rGO ADSORBENTS OVER THE COURSE OF 3120 MINUTES. DASHED LINES EXTRAPOLATED ADSORPTION PROFILES FOR GO\textsubscript{MRH12} AND THE rGO\textsubscript{VC} SPONGE ASSUMING THAT ADSORPTION CAPACITY IS REACHED BY 3120 MINUTES. THE BLUE REGION REPRESENTS THE INITIAL 300 MINUTES OF ADSORPTION WHICH ARE USED TO EXTRAPOLATE FROM. THE GREY REGION REPRESENTS OTHER POSSIBLE EXTRAPOLATIONS, DEPENDANT ON WHEN THE LIMIT IS REACHED. FOR THE 10 mg SAMPLES USED, THE MAXIMUM \( q \) IS APPROXIMATELY 15 mg/g BASED ON THE EXPERIMENTAL SETUP WHICH IS THEREFORE TREATED AS 100%.
While the starting rate is limited by the initial absorption of the dye into the pores of the sponge, once this has occurred the rate of dye adsorption starts to increase. After 3120 minutes (52 hrs), the concentration of RhB dye remaining was measured using UV-Vis as shown in Figure 7.6.3. The rGO$_{VC}$ sponge shows a lower concentration of dye remaining than both GO$_{MRH11}$ and GO$_{MRH12}$ despite the slower initial rate (Figure 7.6.2). This is likely due to an increased adsorption capacity for the rGO$_{VC}$ sponge, compared with GO$_{MRH11}$ and GO$_{MRH12}$, caused by the porous structure of the sponge. The $q_e$ value of 12.1 mg/g for the rGO$_{VC}$ sponge is higher than the $q_e$ value for rGO$_{VC}$ powder of 5.8 mg/g showing the merit of porosity in rGO materials. However, both adsorption capacity and rate of adsorption for the rGO$_{VC}$ sponge are considerably lower than GO$_{MRH13}$ and the rest of the series due the lack of interlayer adsorption potential. It is possible the conclude that while the rGO$_{VC}$ sponge is somewhat easier to handle, due to its compact dimensions and inability to disperse in solution, effectively reducing the amount of residual rGO left after use, which makes it favourable for environmental remediation applications, this comes at a cost to overall adsorption capacity and particularly rate of adsorption.

**Figure 7.6.3** (A) UV-absorption spectra of the GO$_{MRHXX}$ series and the rGO$_{VC}$ sponge after adsorption of RhB dye for 52 hours and (B) digital photographs of the remaining RhB dye after 168 hrs, showing that GO$_{MRH11}$ and GO$_{MRH12}$ have reached adsorption capacity.
7.7 Magnetic Reduced Graphene Oxide Adsorbers

The Fe-rGO material, synthesised and characterised in Chapter 4, presents an interesting method for separating the adsorbent from the adsorbate through the use of magnetic manipulation. 10 mg of Fe-rGO powder was added to a solution of RhB dissolved in water (150μg, 10 ml of 15 mg/L) and the quantity of dye adsorbed measured over 300 minutes in the same way as the GO_{MRHxx} series (Figure 7.7.1). In the experiment, the Fe-rGO material is capable of adsorbing approximately 95% of the dye after 300 minutes. This is slower than the fast adsorbing GO_{MRH13} – GO_{MRH16} which are capable of adsorbing the same amount of dye in less than 30 minutes. However, the Fe-rGO material shows a significant improvement in both adsorption rate, and total adsorption capacity when compared with GO_{MRH11}, GO_{MRH12} and the rGO\_VC sponges. Based on the initial rate of adsorption (0 - 120 mins), the maximum $q_e$ value (possible when the dye is present in excess) is calculated to be 34.1 mg/g which is significantly higher than GO_{MRH11} and GO_{MRH12}.

Furthermore, by substituting the silver resin for an iron resin, iron nanoparticles can be decorated onto the rGO\_VC sponge. The synthesis method for these Fe-rGO sponges is detailed in Section 7.3. By introducing iron nanoparticles into the sponge, it was anticipated that magnetic properties of the iron nanoparticles would transfer to the sponge as a whole. This would allow for magnetic manipulation, creating an easy method of sponge removal from solution after absorption has occurred. Figure 7.7.2 shows SEM images of an rGO\_VC sponge immersed in iron resin then thermally treated to ensure iron nanoparticle formation.
as described in Section 7.3. Image (A) shows an overview of the whole sponge that was used for imaging. The sponge compacts because of the thermal treatment, however pores are still visible as highlighted in (B). The SEM images presented in (C) and (D) show the composition of the sponge is not distorted by the addition of the iron nanoparticles. In the SEM image presented in (D) it is possible to see very small (< 50 nm) iron nanoparticles dispersed across the surface of the rGO sheets.

![Image](image-url)

**FIGURE 7.7.2 SEM IMAGES OF AN Fe-rGO SPONGE AFTER THERMAL TREATMENT. THE SCALE BARS REPRESENT (A) 1 mm, (B) 150 µm, (C) 3 µm AND (D) 2 µm A LARGE VERSION OF (D), HIGHLIGHTING THE IRON NANOPARTICLES ON THE SURFACE CAN BE FOUND IN THE APPENDICES (SECTION 10.8).**

It is interesting to note that the iron nanoparticles do not form large aggregates like the silver particles. This is confirmed by examining the micro-CT images presented in Figure 7.7.3. It is proposed that this is because the iron nitrate is reduced as a result of the thermal treatment, rather than via interaction with vitamin C, as is the case for the silver nitrate. The 3D models in (A) and (B) show that the iron is distributed throughout the whole sponge. Unlike for the silver decorated sponges presented in Section 7.5, the cross section in (C) shows no distinct increase in intensity at the outer surface of the sponge, or around the voids that are present. This is highlighted in the line profile presented in Figure 7.7.4. This is
a good indication that iron nanoparticles are not forming into large aggregates upon contact with the sponge surface. It is therefore, likely that the iron nanoparticles are better dispersed throughout the main body of the sponge while the silver particles are present in higher concentrations around the edges in their respective sponges. It is interesting to note from the line profile that the concentration of silver decreases when approaching the centre of the sponge. This indicates that the iron resin is being adsorbed onto the surface of the sponge, thus lowering the concentration which reaches centre of the sponge. If the sponge was not adsorbing the iron resin, the concentration would remain constant and all areas reached by the resin would have a similar intensity.

![Image]

**FIGURE 7.7.3** 3D MODELS GENERATED FROM MICRO CT X-RAY PROJECTIONS OF rGO$_{VC}$ SPONGES DIPPED IN IRON RESIN (20 mg/mL) PRIOR TO FREEZE DRYING. (A) 3D MODEL IS CONSTRUCTED FROM THE CT DATA (B) SURFACES ARE RENDERED AND SMOOTHED USING THE HIGHEST INTENSITIES AND (C) A CROSS SECTION IS TAKEN. EACH VOXEL REPRESENTS 50 µm$^3$.

![Image]

**FIGURE 7.7.4** LINE PROFILES OF rGO$_{VC}$ SPONGES DIPPED IN IRON RESIN (20 mg/mL) PRIOR TO FREEZE DRYING. THE BLUE BOX IN (A) INDICATES A VOID IN THE SPONGE, WHILE THE ORANGE LINES IN (B) HIGHLIGHT THE DECREASING INTENSITY WHEN APPROACHING THE CENTRE OF THE SPONGE. EACH PIXEL OF THE CROSS SECTION REPRESENTS 50 µm$^2$. 
Upon thermal treatment at 800°C for 2 hours under nitrogen, the adsorbed iron resin is converted into iron nanoparticles which are responsive to magnetic fields. This is demonstrated in Figure 7.7.5 where an rGO_{VC} sponge with iron nanoparticles is picked up with a magnet. This property is important in environmental remediation as it allows for easy removal of the sponge after it has been used to absorb an adsorbate. It is determined that the iron nanoparticles are ferromagnetic by examining the magnetic hysteresis (Figure 7.7.6). The presence of hysteresis in the S shaped curve indicates that when the applied magnetic field is reduced to 0, the material retains a magnetic moment. Therefore, the Fe-rGO material can be classified as ferromagnetic. This results in high enough magnetic susceptibility for the sponge to be picked up using a magnet as shown.

*FIGURE 7.7.5 DIGITAL PHOTOGRAPH OF AN rGO_{VC} SPONGE DECORATED WITH IRON NANOPARTICLES BEING PICKED UP WITH A STIRRING BAR MAGNET. (IMAGES COURTESY OF N. L. V. CARREÑO, FEDERAL UNIVERSITY OF PELOTAS, PELOTAS, BRAZIL).*
The magnetic properties of the Fe-rGO material enable the use of magnetic manipulation to aid in environmental remediation. This could present in many forms, for example, the mobilisation of adsorbent materials to specific target sites, or the use of magnets to hold the adsorbent materials in place. One of the most interesting advantages is in the recovery of adsorbent materials, extraction of the adsorbate molecules and subsequent reuse of the adsorbent. Given the wide range of sorbates, such as petroleum products and organic solvents, that rGO sponges have been shown to sorb in the literature, enhancing sorbate recovery is highly favourable. To this end, 150 μg of RhB dye (10 mL at 15 mg/L in water) was adsorbed onto Fe-rGO (10 mg) over the course of 7 days. Subsequently, the Fe-rGO was held in place using a magnet and the water decanted. The Fe-rGO was subsequently redispersed in 10 mL of ethanol, resulting in desorption of the RhB dye, turning the ethanol pink (Figure 7.7.7). This elution was repeated three more times with the ethanol being decanted and replaced with fresh ethanol to encourage further desorption. Consequently, 75% of the RhB dye adsorbed was desorbed in the first elution, with 99% of the dye desorbed after 4 x 10 mL elutions.
FIGURE 7.7.7 (A) UV-VIS ABSORPTION SPECTRA FOR RhB ELUTED FROM Fe-rGO, AND (B) THE PERCENTAGE OF THE DYE RECOVERED THROUGH EACH SUCCESSIVE ELUTION. THE INSET IMAGE SHOWS THE WATER DECANTED FROM THE ORIGINAL RhB ADSORPTION, AND THE FIRST Fe-rGO ELUTION 1 MINUTE AFTER THE ETHANOL IS ADDED.

To conclude, the Fe-rGO material shows interesting promise for use as an adsorbent material with possible applications in environmental remediation. Initial adsorption properties are shown to be better than GO_{MRH11} and GO_{MRH12}, with a slower rate of adsorption compared with GO_{MRH13} – GO_{MRH16}. However, the inclusion of magnetic properties allows for effective separation of the adsorbent from the solution, limiting the impact of complexation and subsequent cross contamination as is present in more oxidised GO samples. Furthermore, the magnetic properties allow for the separation of the Fe-rGO from solution after adsorbing, which allows for the recovery of target adsorbates through elution. Moreover, Fe-rGO sponges have been synthesised which show a uniform distribution of iron nanoparticles throughout the sponge, which subsequently provides magnetic properties to the porous sponge material. Considering the wide variety of materials that rGO sponges have been shown capable of adsorbing in literature, it is highly likely that these Fe-rGO sponges would be capable of adsorbing, and more importantly recovering, a similar range of materials.

7.8 SUMMARY
In this chapter, the adsorption properties of various GO materials were showcased for use in environmental remediation applications. The GO_{MRHxx} series was used to determine the optimum degree of oxidation required for adsorption of the fluorescent dye RhB. It was shown that all the GO_{MRHxx} series are capable of adsorption although with different degrees of effectiveness. This adsorption effectiveness is correlated to the interlayer distance...
measured by XRD in Chapter 4. GO samples with a reduced interlayer distance similar to graphite (GO_{MRH11} and GO_{MRH12}) exhibited significantly slower adsorption properties when compared with more oxidised GO samples with larger interlayer distances. As shown in Chapter 4, samples with the larger interlayer distance are capable of trapping water between the GO layers, and therefore it is proposed that the adsorption rate is greatly increased as interlayer adsorption is enabled.

However, the increased oxidation in GO samples leads to a higher dispersability and solution stability, which consequently stays present in the solution, effectively cross contaminating the solution with GO. For GO_{MRH15} and GO_{MRH16} this is seen to be the case, with a GO-RhB complex remaining present and stable in the solution. Therefore, from the GO_{MRHxx} series, GO_{MRH13} was determined to be the most effective, as it showed the ability to adsorb the dye quickly but did not remain stable in the solution, leading to a lower total absorption across the visible spectrum for the solution after adsorption.

To counter the likelihood of cross contamination from GO-RhB complexation, porous rGO_{VC} sponges were synthesized to compare with the GO series. SEM imaging is used to highlight the porous structure, while contrast micro CT is used to confirm 3D porosity, through the adsorption of silver particles throughout the sponges. The micro CT images also highlight interesting features in the sponges, including empty voids present within the 3D structure, and aggregation of silver particles formed on contact with the sponge. Raman analysis of the sponges suggest a partial reduction may have occurred which might lead to better adsorption profiles when compared with fully reduced rGO samples. However, the rGO_{VC} sponges demonstrate lower adsorption effectiveness when compared with GO_{MRH13} – GO_{MRH16}, although without the possibility for contamination through complexation. The reduced adsorption properties provide further evidence that interlayer adsorption is occurring in GO_{MRH13} – GO_{MRH16}, given the graphite-like interlayer distance of rGO_{VC}.

Finally, magnetic Fe-rGO material is used as an adsorbent material, showing higher adsorption effectiveness than GO_{MRH11} and GO_{MRH12}, but not as high as the interlayer adsorbing GO_{MRH13} – GO_{MRH16}. Additionally, Fe-rGO sponges are synthesised, which show uniform distribution of iron nanoparticles throughout the 3D structure. The magnetic properties of both Fe-rGO and Fe-rGO-based sponges unlock many possible advantages,
including the ability to easily recover adsorbed materials through magnetic manipulation of the material. This is demonstrated through the elution of RhB from Fe-rGO with 99% of the initial dye concentration recovered after 4 elutions. Therefore and in conclusion, while GO$_{MRH13}$ is shown to be the most effective at adsorbing RhB dye, specific applications may be better suited to either the rGO$_{VC}$ sponges, or the magnetically manipulatable Fe-rGO.
8 CONCLUSIONS AND FUTURE WORK

8.1 CONCLUSIONS

This thesis has provided a detailed characterisation of the graphene like GO and rGO materials, investigating the extent to which these materials can vary depending on the extent of the oxidation, and in the case of rGO, the type of reduction method used. It subsequently investigated some of the many uses of GO and rGO, including as a hole transport layer in OPV devices, as a transparent conducting electrode, and as an adsorbent material for environmental remediation. It also characterised and utilised Fe-rGO, a magnetic rGO material with great potential for future exploitation.

Through the GO_{hmx} series presented in Chapter 3, it was demonstrated that increasing sized batches of GO can be synthesised without detrimentally affecting the final product. This is essential for the potential mass production of GO for use in future applications. Therefore, given the cheap cost of the starting materials required (i.e. graphite) the utilisation of GO, for example, as a charge transport in OPV’s, could lead to a significant reduction in costs. Comparing the price of PEDOT:PSS, £1499.90 per L (£149.99 per 100 mL x 10$^{177}$, and GO, at the optimum concentration for OPV via spin coating determined in Chapter 5, £282.40 per L at 2 mg/mL, ($1000 per L at 5 mg/mL$^{178}$ the cost reduction in materials alone is substantial. Additionally, by changing the starting synthesis conditions, it is possible to tune the GO material to better suit specific applications, for example, the adsorbent membranes presented in Chapter 7.

Commonly, when investigating graphene based materials, the Raman $I_D/I_G$ ratio is used as the sole measure of disorder. However, given the wide range of disorder stages possible between pristine graphite and GO, it is sometimes ineffective to exclusively use to the $I_D/I_G$ ratio as a measure of disorder, specifically for samples with high levels of disorder such as GO. By supplementing the $I_D/I_G$ ratio with the FWHM$_D$ and FWHM$_G$ peaks, it is possible to successfully determine level of structural disorder more accurately, allowing GO and rGO samples to be compared. The small FWHM$_D$ and FWHM$_G$ for rGO$_{VC}$ (66 ± 6 cm$^{-1}$ and 59 ± 4 cm$^{-1}$ respectively), coupled with an $I_D/I_G$ ratio of 1.17 ± 0.02, shows the least disorder, making it more suitable for electrical applications. Alternatively, the large FWHM$_D$ and FWHM$_G$ of rGO$_{Sol}$ (168 ± 2 cm$^{-1}$ and 84 ± 1 cm$^{-1}$ respectively) coupled with an $I_D/I_G$ ratio of 0.73 ± 0.02 suggests a high level of disorder. This method of structural disorder estimation
can be confirmed by examining the thermal decomposition temperature in air of the GO/rGO materials.

GO films were tested in OPV devices as an alternative hole transport layer to PEDOT:PSS. Devices incorporating GO demonstrated efficiencies similar to PEDOT:PSS (∼5% for both using active layer blend of PCDTBT:PC$_{70}$BM). Given the deep HOMO level of PCDTBT (5.5 eV), the similar efficiencies of GO based devices demonstrate that GO can be used as a hole transport layer material for a wide range of polymer active layers. As a result of the chemical stability of the GO compared to PEDOT:PSS, lifetime tests estimate a 62% longer shelf lifetime for OPV’s using GO as an alternative to PEDOT:PSS. This is vital for tackling the short lifetime currently experienced by OPV devices, which hinder their progress as a cheap, easy to mass produce alternative source of renewable energy.

A method of low temperature “on surface” chemical reduction of GO films using vitamin C was developed, capable of producing conductive thin films, without the need for substrate treatment or the high temperatures required in CVD grown graphene. A conductivity ratio ($\sigma_{DC}/\sigma_{Op}$) of 0.046 is similar to other rGO flake based conducting networks seen in literature. While not currently competitive with ITO, evidence suggests that the conductivity of the individual rGO flakes themselves are not limiting the conduction through the film, rather conduction is limited by charge transport between rGO flakes. This highlights the direction future research should follow, with improving the junctions between flakes a top priority, in order to successfully develop a cheap and effective alternative to ITO to keep up with the ever increasing demand.

As an environmental membrane, a range of GO materials were tested for the adsorption of the textile dye RhB, and compared with vitamin C reduced GO 3D porous sponge structures. Using SEM and X-ray CT scanning, coupled with the absorption of metal nanoparticles to provide contrast, the sponges were reconstructed, and shown to be porous and effective absorbers throughout. However, increased adsorption was observed for more oxidised GO samples compared to the less oxidised samples, with over 80 mg RhB dye adsorbed per gram of GO in 300 minutes for all moderately oxidised samples. Analysis of the interlayer distance, as measured by XRD, for the more oxidised GO samples demonstrate an increase from $\approx 3.35\text{Å}$ to 9Å, which it is proposed enables the ingress of solution between the layers,
which therefore aids adsorption. Adversely, it is demonstrated that the most oxidised GO samples show evidence of complexation with the dye, making isolation from solution difficult. The most oxidised samples also remain stable in solution longer resulting in a 10 times higher concentration of GO after 52 hours without agitation. Therefore, a trade-off is seen, in which GO that is sufficiently oxidised enough to increase the interlayer distance, but not oxidised enough to remain stable in solution, is shown to be optimum for adsorption applications.

Finally, a new magnetic rGO hybrid was produced through decoration and impregnation of iron nanoparticles into the rGO sheets. This magnetic variant of rGO is shown to have a lower work function when compared to standard GO, which results in a higher $V_{oc}$ in test PCDTBT:PC$_{70}$BM OPV devices. Also, the Fe-rGO variant can be used to adsorb RhB and subsequently it is demonstrated that it can be easily removed from solution post adsorption and the dye desorbed through elution. This is important given the wide variety of materials the GO/rGO materials are capable of adsorbing, potentially allowing for easy and effective recovery of various adsorbates. One of the significant challenges for the future is the stabilisation of Fe-rGO in solution, which would not only allow for its properties in OPV to be fully realised, but which also unlocks various other potential applications including the magnetic alignment of deposited thin films.

To conclude, this thesis has demonstrated a range of possible applications that solution processable GO and rGO based interfaces can be used in, covering applications such as energy generation, electronic conduction and environmental membranes. The wide variety of tuneable properties associated with GO and rGO, coupled with numerous ways of functionalization (as demonstrated by Fe-rGO and the rGO sponges), make it a great platform material, capable of being adapted to suit a wide variety of applications.

8.2 Future Work

The work presented in this thesis prompts a range of possible avenues for future investigation. Following the detailed characterisation of GO materials synthesised using differing concentrations of potassium permanganate, it would be interesting to investigate the effect the increased potassium permanganate concentration has on electrical properties, such as the work function of the materials. Measuring thin films of the GO$_{MRHxx}$
series using techniques such as ultraviolet photoelectron spectroscopy would be useful as it could lead to further insight into how the properties of GO interfacial layers in devices such as OPVs influence the device performance parameters. For example, if the work function of GO can be lowered further through increased oxidation, it could allow GO to be used successfully as a highly effective hole injection layer in organic light emitting diodes.

Chapter 3 highlights what happens during the oxidation process for GO production in terms of disorder and sp\(^2\) cluster size. It would be advantageous to develop a wider variety of samples, ranging from the starting graphite all the way through to fully oxidised GO, to extend the range shown by the trend. This could allow for the changes in \(I_D/I_G\), FWHM\(_D\), FWHM\(_G\) and thermal decomposition temperature in air to be mapped throughout the oxidation process, creating an oxidation scale for GO materials. This could also be extended to include GO reduction methods, which would allow for a definitive measure of how each reduction method progresses. For example, through analysis of the G peak position, it can be determined whether a reduction method works by increasing sp\(^2\) cluster sizes, or by connecting existing clusters through sp\(^2\) chain formation. This is essential for improving the understanding of the reduction process as a whole, and could give clarity to which reduction method is best suited for specific applications.

Regarding applications, the continued development of OPV technology is necessary to its future implementation. The lifetime tests presented show that the use of GO in OPV resulted in increased internal stability. It would be interesting to confirm whether this is due to the chemically neutral properties of GO in comparison to the acidic PEDOT:PSS. This could be achieved by running depth profiles of degraded devices, using techniques such as X-ray Photoelectron Spectroscopy, or Time-of-Flight Secondary Ion Mass Spectrometry, to track the diffusion of indium into the OPV devices. By comparing the diffusion of indium into that active layer for different hole transport layers, including GO and PEDOT:PSS, it could be shown to what extent the acidity of the hole transport layer catalyses this process, or whether indium diffusion is blocked by certain hole transport layers. This is important for establishing the necessary criteria for an effective hole transport layer material in long lifetime OPV devices.
The development of solution processable thin film rGO as an alternative to the transparent conducting electrode material, ITO, is a continuing avenue for future research. Analysis of deposited thin films of rGO$_{VC}$ suggest that a major limiting factor for conductivity is the junctions between flakes. Therefore to increase conductivity, it may be necessary to lower the number of junctions. This could be assessed by comparing GO materials with different flake sizes, and their subsequent effect on final film conductivity. Depending on the size of the flakes produced, this could lead to an increase in the suggested conductivity limit for solution processed flake based rGO networks. Another possibility is the development of conductivity flake interconnects, allowing for high conductivity charge transport between flakes, which could increase electrical conductivity and result in rGO networks being competitive with ITO counterparts. Producing a high conductivity rGO ink could be instrumental in developing various cheap flexible electronics, driving flexible electronics technology forward.

The development of a magnetic Fe-GO material, combining the magnetic properties of Fe-rGO with the solution process ability of GO, could potentially result in improvements to both OPV and adsorption applications. It would also allow for the deposition of Fe-GO on a substrate in tandem with a reducing agent (i.e. vitamin C) to enable unaggregated Fe-rGO films. This could prove important for OPV applications, as the change in work function has already shown that efficiency could be improved through the use of Fe-rGO. A suitable layer of Fe-rGO as a replacement for PEDOT:PSS could also show improved lifetime properties in air, as the hydrophobic nature of the Fe-rGO could limit water’s ability to enter the device, thus lengthening the lifetime. Additionally, adsorption studies undertaken in this thesis suggest that a Fe-GO material could capitalise on the adsorption properties of GO without the fear of cross contamination. Initial attempts to re-oxidise Fe-rGO to produce Fe-GO proved unsuccessful, with magnetic properties being lost as the impregnated iron nanoparticles are lost as the layers separate. Therefore, alternative methods of producing a Fe-GO material would be an avenue of future work worth exploring.

Furthermore, the incorporation of other types of metallic nanoparticles to GO/rGO could unlock new and exciting properties. The incorporation of specific sized gold nanoparticles into GO could provide plasmonic effects for improving the efficiency of OPV devices. The addition of other metal nanoparticles to the rGO sponges also open up a wide variety of
options for possible exploitation. For example, Chapter 7 demonstrated the possibility for incorporation of silver metal nanoparticles into the structure of the rGO sponges. This could be used as a water filter with added antibacterial properties, which could be helpful for providing clean water in remote locations.

In terms of adsorbent materials, with an understanding of the optimum properties for a GO based adsorbent material, it is essential that the adsorption properties are compared with commercially available adsorbent materials, in order to establish their overall effectiveness. Additionally, it would be worth exploring the sorption properties of GO materials when sorbing other sorbates, such as petroleum products. Initial tests and literature sources suggest the absorption of petroleum products is possible through the use of rGO sponges. Coupled with the magnetic properties of materials such as Fe-rGO, this could lead to the development of an improved method for oil spill recovery, which could revolutionise the response to such environmental disasters. The feasibility of this is demonstrated in Figure 8.2.1, which shows an Fe-rGO sponge absorbing oil, before the sponge is removed and the oil inside ignited.

![Figure 8.2.1](image_url)

*FIGURE 8.2.1 (LEFT) ABSORPTION OF DIESEL IN WATER USING THE Fe-rGO SPONGE, AND (RIGHT) SUBSEQUENT BURNING OF THE ABSORBED DIESEL.
(IMAGES COURTESY OF N. L. V. CARREÑO, FEDERAL UNIVERSITY OF PELOTA, PELOTA, BRAZIL)*
9 REFERENCES


de Jong, M. P., van Ijzendoorn, L. J. & de Voigt, M. J. A. Stability of the interface between indium-tin-oxide and poly(3,4-
ethylenedioxythiophene)/poly(styrenesulfonate) in polymer light-emitting diodes. 


## 10 Appendices

### 10.1 IR Comparison Table

**Table 10.1-1 Correlation Table Used to Assign Absorption Peaks to Functional Groups for IR Spectroscopy as Used in Section 3.7 and Section 4.7.**

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<td></td>
<td>Alcohol O–H stretching</td>
</tr>
<tr>
<td>3550–3500</td>
<td>Phenol O–H stretching</td>
</tr>
<tr>
<td>1300–1000</td>
<td>C–O stretching</td>
</tr>
<tr>
<td></td>
<td>Ethers</td>
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<tr>
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<td>C–O–C stretching</td>
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<td>2900–2700</td>
<td>Aldehydes and ketones</td>
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<td>Aromatic ketone C=O stretching</td>
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<td>Out-of-plane C–H bending</td>
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10.2 XRD Peak Assignments for the GoMRHxx Series

**Table 10.2-1** XRD Peak Assignments for the Major Peaks in the GoMRHxx Series and FWHM Values Used in the Scherrer Equation, Presented in Section 3.5.

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10.3 Hansen Solubility Parameters

**Table 10.3-1** List of Hansen Solubility Parameters with Calculated Hildebrand Parameters.

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<th>Solvent</th>
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<th>$\delta_T (\text{MPa}^2)$</th>
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<td>Water</td>
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<td>Iso-propanol (IPA)</td>
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<td>5.3</td>
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</tr>
<tr>
<td>Acetone</td>
<td>15.5</td>
<td>10.4</td>
<td>7.0</td>
<td>19.9</td>
</tr>
<tr>
<td>2-Butanol (2-But)</td>
<td>15.8</td>
<td>5.7</td>
<td>14.5</td>
<td>22.2</td>
</tr>
<tr>
<td>Chloroform</td>
<td>17.8</td>
<td>3.1</td>
<td>5.7</td>
<td>18.9</td>
</tr>
<tr>
<td>Diethyl Ether</td>
<td>14.5</td>
<td>2.9</td>
<td>4.6</td>
<td>15.5</td>
</tr>
<tr>
<td>Ethanol (EtOH)</td>
<td>15.8</td>
<td>8.8</td>
<td>19.4</td>
<td>26.5</td>
</tr>
<tr>
<td>Ethylene Glycol</td>
<td>17.0</td>
<td>11.0</td>
<td>26.0</td>
<td>33.0</td>
</tr>
<tr>
<td>Methanol (MeOH)</td>
<td>14.7</td>
<td>12.3</td>
<td>22.3</td>
<td>29.4</td>
</tr>
<tr>
<td>N-Methyl-2-Pyrrolidone (NMP)</td>
<td>18.0</td>
<td>12.3</td>
<td>7.2</td>
<td>23.0</td>
</tr>
<tr>
<td>N,N-Dimethyl Formamide (DMF)</td>
<td>17.4</td>
<td>13.7</td>
<td>11.3</td>
<td>24.9</td>
</tr>
<tr>
<td>Ortho-Dichlorobenzene (o-DCB)</td>
<td>19.2</td>
<td>6.3</td>
<td>3.3</td>
<td>20.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.0</td>
<td>1.4</td>
<td>2.0</td>
<td>18.2</td>
</tr>
<tr>
<td>Graphene Oxide (GO)</td>
<td>17.5</td>
<td>10.0</td>
<td>15.7</td>
<td>25.4</td>
</tr>
<tr>
<td>Reduced Graphene Oxide (rGO)</td>
<td>17.9</td>
<td>7.9</td>
<td>10.1</td>
<td>22.0</td>
</tr>
<tr>
<td>Graphene (GO)</td>
<td>18.0</td>
<td>9.3</td>
<td>7.7</td>
<td>21.7</td>
</tr>
</tbody>
</table>
10.4 Contact Angle Measurements
Contact angle measurements were taken by depositing a set volume (0.1mL) of water onto a substrate (silicon or plastic substrate acrylonitrile butadiene styrene). Images are taken using a high quality camera, and the angle between the surface and the water droplet measured as shown in Figure 10.4.1. Contact angle measurements are useful for determining the hydrophobicity of a surface, with hydrophobic surfaces forming droplets with larger contact angles.

![Contact Angle Measurements](image)

**Figure 10.4.1** Contact Angle Measurements for (Top) Water on a Silicon Substrate and (Bottom) Water on an Acrylonitrile Butadiene Styrene Substrate. The Difference in Colour of the Water Droplet is a Reflection of the Substrate Colour.
**10.5 Conduction Mechanism Derivations**

Derivation of the Poole Frenkel Equation – For use in electrical conduction mechanism plots

\[ J = e \mu n_0 E \exp \left( -\frac{\phi_w - e \beta_{PF} E^2}{kT} \right) \]

\[ \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \]

Starting Equation

\[ \frac{J}{e \mu n_0 E} = \exp \left( -\frac{\phi_w - e \beta_{PF} E^2}{kT} \right) \]

\[ \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \]

Divide by \( A^*T^2 \)

\[ \ln \left( \frac{J}{e \mu n_0 E} \right) = -\left( \frac{\phi_w - e \beta_{PF} E^2}{kT} \right) \]

\[ \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \]

Take Natural Log (ln)

\[ \ln \left( \frac{J}{e \mu n_0 E} \right) = e \frac{\beta_{PF}}{kT} \times E^2 \frac{1}{2} - \frac{\phi_w}{kT} \]

\[ \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \]

Translate to \( y = mx + c \)

\[ \ln \left( \frac{J}{e \mu n_0 E} \right) = e \frac{\beta_{PF}}{kT} \frac{E^2}{2} - \frac{\phi_w}{kT} \]

\[ \beta_{PF} = \left( \frac{e}{\pi \varepsilon_0 \varepsilon_r} \right)^{\frac{1}{2}} \]

Take \( \frac{dy}{dx} \)

\[ \frac{\frac{1}{2}}{\frac{1}{1} + \frac{1}{2} + \frac{1}{3}} = A \frac{\beta_{Sch}}{m^2 k g} - \frac{1}{k g \frac{2}{m^2 k g} \frac{1}{2} + \frac{1}{1} + \frac{1}{2} + \frac{1}{3}} \]

\[ \beta_{PF} = \left( \frac{A}{A^* \lambda^4 k g} \right)^{\frac{1}{2}} \]

SI Base Units

\[ \frac{1}{k g \frac{1}{m^2 k g} \frac{1}{2} + \frac{1}{2} + \frac{1}{3}} = A \frac{\beta_{Sch}}{m^2 k g} - \frac{1}{k g \frac{2}{m^2 k g} \frac{1}{2} + \frac{1}{1} + \frac{1}{2} + \frac{1}{3}} \]

\[ \beta_{PF} = k g \frac{1}{m^2 k g} \frac{1}{2} + \frac{1}{1} + \frac{1}{2} + \frac{1}{3} \]

Cancelling out

\[ k g \frac{1}{m \frac{1}{A^2 s^2}} = A \frac{A \frac{1}{k g} \frac{1}{m^2 k g} \frac{1}{2} + \frac{1}{1} + \frac{1}{2} + \frac{1}{3}}{k g \frac{1}{m^2 k g} \frac{1}{2} + \frac{1}{1} + \frac{1}{2} + \frac{1}{3}} \]

Putting in \( \beta_{Sch} \)

\[ k g \frac{1}{m \frac{1}{A^2 s^2}} = k g \frac{1}{m \frac{1}{A^2 s^2}} - k g \frac{1}{m \frac{1}{A^2 s^2}} \]

Units Match (Final Proof)
Derivation of the Schottky Equation – For use in electrical conduction mechanism plots

\[ J = A^*T^2 \exp \left( -\frac{\phi_w - e\beta_{Sch}E^2}{kT} \right) \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{e}{4\pi\epsilon_0\epsilon_r} \right)^{\frac{1}{2}} \]

\[ \frac{J}{A^*T^2} = \exp \left( -\frac{\phi_w - e\beta_{Sch}E^2}{kT} \right) \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{e}{4\pi\epsilon_0\epsilon_r} \right)^{\frac{1}{2}} \]

\[ \ln \frac{J}{A^*T^2} = \ln \left( \exp \left( -\frac{\phi_w - e\beta_{Sch}E^2}{kT} \right) \right) \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{e}{4\pi\epsilon_0\epsilon_r} \right)^{\frac{1}{2}} \]

\[ \ln \frac{J}{A^*T^2} = \frac{e\beta_{Sch}}{kT} \times \frac{E^2 - \phi_w}{kT} \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{e}{4\pi\epsilon_0\epsilon_r} \right)^{\frac{1}{2}} \]

\[ \frac{\ln \frac{J}{A^*T^2}}{E^2} = \frac{e\beta_{Sch}}{kT} - \frac{\phi_w}{kT} \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{e}{4\pi\epsilon_0\epsilon_r} \right)^{\frac{1}{2}} \]

\[ \frac{\frac{A_m m^{-2} K^{-2} Kg^{-2}}{kg m^2 A^{-1} s^{-2}}}{\frac{As}{m^2 kg s^{-2} K^{-1} K^{-1}}} = \frac{\frac{As\beta_{Sch}}{m^2 kg s^{-2} K^{-1} K^{-1}}}{kg m^2 A^{-1} s^{-2} m^{-2} s^{-2}} \]

\[ \Rightarrow \beta_{Sch} = \left( \frac{As}{A^2 s^4 kg^{-1} m^{-3}} \right)^{\frac{1}{2}} \]

\[ \frac{1}{kg m^2 A^{-1} s^{-2}} = \frac{As^3 \beta_{Sch}}{m^3 kg} - \frac{1}{kg m^2 A^{-1} s^{-2}} \]

\[ \Rightarrow \beta_{Sch} = k g \frac{1}{m^3 A^2 s^3} \]

\[ \frac{k g m^{-2} A^{-1} s^{-3}}{m^2 kg} = \frac{As^3 k g m^2 A^{-1} s^{-3}}{m^2 kg} - \frac{k g m^{-2} A^{-1} s^{-3}}{m^2 kg} \]

\[ \Rightarrow \beta_{Sch} = k g \frac{1}{m^3 A^2 s^3} \]

\[ k g \frac{1}{m^2 A^{-1} s^{-2}} = k g \frac{1}{m^3 A^2 s^2} = k g \frac{1}{m^3 A^2 s^2} - k g \frac{1}{m^3 A^2 s^2} \]

Units Match (Final Proof)
Derivation of the Fowler Nordheim Equation – For use in electrical conduction mechanism plots

\[ J = C_1E^2 \exp\left(\frac{-\kappa}{E}\right) \]

\[ \frac{J}{C_1E^2} = \exp\left(\frac{-\kappa}{E}\right) \]

\[ C_1 = \frac{e^3}{32\pi^3 h \varphi_w} \]

\[ -\kappa = \frac{8\pi(2m^*)^{0.5}}{3eh} \varphi^{1.5} \]

Starting Equation

Divide by \( C_1E^2 \)

\[ \ln\left(\frac{J}{C_1E^2}\right) = \frac{-\kappa}{E} \]

\[ C_1 = \frac{e^3}{32\pi^3 h \varphi_w} \]

\[ -\kappa = \frac{8\pi(2m^*)^{0.5}}{3eh} \varphi^{1.5} \]

Take Natural Log (ln)

Translate to \( y = mx \)

\[ \ln\left(\frac{J}{C_1E^2}\right) = -\kappa \times \frac{1}{E} \]

\[ C_1 = \frac{e^3}{32\pi^3 h \varphi_w} \]

\[ -\kappa = \frac{8\pi(2m^*)^{0.5}}{3eh} \varphi^{1.5} \]

Take \( \frac{dy}{dx} \)

\[ \frac{A m^{-2}}{C_1 kg^2 m^4 A^{-2} s^{-6}} = -\kappa \]

\[ C_1 = \frac{A^3 s^3}{kg.m^2 s^{-1} kg.m^2 s^{-2}} \]

\[ -\kappa = \frac{k^2}{A.s kg m^2 s^{-1}} k^2 g^2, m^3 s^{-3} \]

SI Base Units

Cancelling out

\[ \frac{A^3 s^6 m^{-4} k g^{-2}}{C_1 kg^{-1} m^{-1} A s^3} = -\kappa \]

\[ C_1 = A^3 s^6 m^{-4} k g^{-2} \]

\[ -\kappa = k g^1, m^1 A^{-1} s^{-3} \]

Putting in \( C_1 \) and \(-\kappa\)

\[ \frac{A^3 s^6 m^{-4} k g^{-2}}{kg^{-1} m^{-1} A s^3} = k g^1, m^1 A^{-1} s^{-3} \]

Units Match (Final Proof)

\[ k g^1, m^1 A^{-1} s^{-3} = k g^1, m^1 A^{-1} s^{-3} \]
10.6 Additional Reduced Graphene Oxide Raman Spectra

Figure 10.6.1 show the Raman spectra for GO solution spray coated into thin films ($t_{ref}$) and annealed at 100°C, 200°C and 250°C respectively as detailed in Section 6.3. Figures 10.6.2 – 10.6.3 show the Raman spectra when vitamin C and GO are spray coated together into thin films and subsequently measured as deposited ($t_0$), or left to reduce in solution for 1 ($t_1$) or 2 ($t_2$) days.
FIGURE 10.6.2 RAMAN SPECTRA FOR GO\textsubscript{VC} FILMS (t\textsubscript{0}) BEFORE AND AFTER HEATING TO 100, 150 AND 250°C

FIGURE 10.6.3 RAMAN SPECTRA FOR GO\textsubscript{VC} FILMS (t\textsubscript{1}) BEFORE AND AFTER HEATING TO 100, 150 AND 250°C
10.7 Reduced Graphene Oxide Sponge Contrast CT Scan

To establish the amount of x-ray absorption by the silver particles in comparison to the carbon sponge, a within-sample contrast reference was synthesised as described in Section 7.3. By only exposing one side of the sponge to the silver resin (a), a portion of the carbon sponge remains unexposed. This contrast reference is shown in Figure 10.7.1. The 3D models, presented in (b) and (c), show that the silver particles are primarily on the surface of the sponge which came into contact with the silver resin. It is interesting to note that not much silver makes it past the sponge surface, instead forming aggregates on the surface. This aggregation likely blocks the pores, restricting access to the rest of the sponge. The large void where the silver has formed is caused by the sponge surface resting on the bottom of the glass vile, which stops silver resin reaching the whole surface area of the carbon sponge. This is demonstrated by the schematic shown in (a) and visible in the cross section presented in (d). The cross section in (d) shows a faint outline caused by the rest of the sponge which provides a reference to the other samples.

![Figure 10.6.4: Raman Spectra for GO\textsubscript{VC} Films (t\textsubscript{2}) before and after heating to 100, 150 and 250\textdegree{}C](image)
FIGURE 10.7.1 3D MODELS GENERATED FROM MICRO CT X-RAY PROJECTIONS OF rGO\textsubscript{VC} SPONGES DIPPED IN 200\mu L SILVER RESIN (20 mg/mL) TO ACT AS A CONTRAST REFERENCE. (a) SHOWS A SCHEMATIC REPRESENTATION OF THE DIPPING SETUP. A 3D MODEL IS CONSTRUCTED FROM THE CT DATA (b), SURFACES ARE RENDERED AND SMOOTHED USING THE HIGHEST INTEENSITIES (c) AND A CROSS SECTION IS TAKEN (d).
10.8 ADDITIONAL IMAGES OF IRON NANOPARTICLE — REDUCED GRAPHENE OXIDE

FIGURE 10.8.1 (TOP) SEM IMAGE OF Fe-rGO AND (BOTTOM) TEM IMAGES OF IRON NANOPARTICLES IMPREGNATED INTO rGO SHEETS. THE TOP IMAGE IS PREVIOUSLY SEEN IN SECTION 7.7, AND IS ENLARGED TO HIGHLIGHT THE PRESENCE OF IRON NANOPARTICLES ON THE SURFACE.