

Graphene-Based Sensors for Soil Analysis: A Spectroscopic and Theoretical Study

Negar Mansouriboroujeni

200203713

Supervised by: Dr. A. Chauvet and Dr. N. Martsinovich

A thesis submitted in partial fulfilment of the requirements for the degree of Doctor of Philosophy

October 2024

Faculty of Science

Department of Chemistry



My Watercolour Interpretation of a Soil Sensor, in a Farm, Monitoring Phosphate Levels Using Oxygen-Functionalized Graphene. Inspired by the Signals in the Soil (SitS) Project.

"Art is the queen of all sciences communicating knowledge to all the generations of the world"

Leonardo Da Vinci

ABSTRACT

This PhD research investigates the electronic and photophysical properties of graphene and its derivatives, focusing on the relationship between these properties and structures of functionalised graphene materials for their potential application in phosphate sensors for agricultural soil analysis as part of the Signals in the Soils (SitS) project. Graphene-based materials were synthesised by our partners within the SitS project, and this study aimed to explore their structural and electronic characteristics which can influence their performance in sensors. Gaining an understanding of the relationship between functionalised graphene's structure and properties helps address a critical gap in the field of nanomaterials to enable their application in sensor technologies.

A combination of ultrafast spectroscopy and computational modelling techniques was employed to investigate functionalised graphenes' structure-property relationship. Experimental methods, including ultraviolet-visible spectroscopy, infrared spectroscopy, and X-ray photoelectron spectroscopy (XPS), were used to investigate the structural and bonding characteristics of graphene-based materials. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) provided key insights into the morphology, particle shape, and particle size distribution of the materials. Transient absorption spectroscopy (TAS) enabled the study of electron dynamics on ultrafast timescales, revealing the impact of oxygen-induced trap states. Density Functional Theory (DFT) simulations using the SIESTA software were conducted to model the electronic and optical properties of these materials and the influence of multiple factors on these properties.

This research showed that electron dynamics in functionalised graphene is a complex process involving multiple decay pathways on a range of timescales. Moreover, this research demonstrated presence of oxygen groups and morphological changes in functionalised graphene. Charge dynamics was found to be directly dependent on the functionalisation of graphene, in particular, on the amount of oxygen present in the samples. The study also showed that oxygen content affects the optical absorption and prolongs carrier lifetimes. Theoretical calculations revealed that oxygen functionalisation, particularly the introduction of hydroxyl and epoxide groups, has a significant impact on the electronic properties of graphene by opening bandgaps. This tunability enhances graphene's optoelectronic properties, making it a promising candidate for sensor applications.

Overall, this research advances the understanding of how oxygen functional groups alter the morphology, electronic structure, and optical properties of graphene, offering new avenues for tailoring its properties for next-generation electronic and sensing devices. The combination of experimental techniques and theoretical modelling provides valuable insights into the design and optimisation of graphene-based materials for technological applications.

TABLE OF CONTENTS

	Page
Abstract	IV
Dedication	VI
Acknowledgement	VII
Conferences, Presentations and Published Work	VIII
Chapter 1. Introduction	1
Chapter 2. Photochemistry, Spectroscopy and Experimental Techniques	44
Chapter 3. Computational chemistry, Quantum Mechanics, and Theoretical Methods.	75
Chapter 4. Optoelectronic Properties and Characterisation of Graphene and Aerosol Gel Graphene Films	101
Chapter 5. Computational Modelling of Graphene-Based Materials	178
Chapter 6. A Comparative Analysis of Experimental and Computational Results on Graphene-Based Materials	235
Chapter 7. Conclusion	246
Chapter 8. Future Work	256
Chapter 9. Additional Research Projects on Metal-oxides, Graphitic, and Molecular	261
Materials Projects	201
Chapter 10. Appendix.	268

DEDICATION

I dedicate my thesis first to my parents for their unwavering support and love. Secondly, to the courageous women of Iran, whose bravery and fiery spirit inspire me. Thirdly, to the women of Afghanistan, whose plight and deprivation of the right to education I will never forget.

ACKNOWLEDGEMENT

I have been fortunate to have met some truly amazing people during my PhD and to have taken part in a variety of extracurricular activities alongside my research, which have truly fuelled my multipod brain. I am forever grateful for the knowledge I gained at Sheffield and the wonderful experiences I had along the way.

I am extremely grateful to my supervisors, **Dr Natalia Martsinovich** and **Dr Adrien Chauvet**, for their guidance, support, and encouragement throughout my PhD journey. Their insights and expertise have been invaluable to my research.

I extend my heartfelt thanks to the postdoctoral researchers who have assisted me, particularly **Dr Alex Auty**, **Dr Xue Yong**, **Dr Joseph Flitcroft** and **Dr Sayantan Bhattacharya**. Your knowledge and assistance have been crucial to the progress of my work. I am grateful to my collaborators, soon to be Dr **Thiba Nagaraja** and **Dr Suprem Das** from Kansas State University, for providing the samples, their assistance with SEM and Raman measurements, and all the SitS members who have played a role in my project.

I gratefully acknowledge the Engineering and Physical Sciences Research Council (EPSRC) for funding my PhD. The computational resources provided by the SHARC, STANAGE, and SOL computer clusters, at The University Of Sheffield (TUOS), as well as ARCHER2, have been essential to my research. Special thanks to the Lord Porter Laser Labs (TUOS) and everyone at ULS Sheffield, particularly to Prof. Julia Weinstein, Dr Robert Oliver, Dr James Pidgeon and Dr Martin Appleby for their support and assistance. I appreciate the technical support from Dr Dimitri Chekulaev (TUOS/Lord Porter Labs), Dr Debbie Hammond (XPS, TUOS), and John Nutter from the Henry Royce Institute (TEM, TUOS). Your expertise has been instrumental in my research.

I also extend my gratitude to the **British Carbon Group** for welcoming me as a member and providing an outstanding conference experience at **Carbon22**, where I had the honour of meeting a personal hero of mine, Nobel Prize winner **Prof. Novoselov** and presenting my work to a distinguished audience.

I would also like to acknowledge my PhD buddy and day-one supporter, future Dr **Ben Smith**, for his camaraderie, with a special thanks to **Dr Samantha Peralta**, who encouraged and motivated me in moments of doubt.

Finally, I would like to thank my loved ones, particularly my parents, **Majizheh Kiani** and **Bahram Mansouri**, and my brother **Arash Mansouri**, for their help, patience, and belief in me throughout all of this. And to my cats, **Saam** and **Cleo**, who have been my companions through it all, I truly would not be here without you.

CONFERENCES, PRESENTATIONS AND PUBLISHED WORK

Conferences

Faraday Joint Conference 2021

29th of March 2021

At the University of Sheffield (Virtual)

Carbon22

3rd to 8th of July 2022

Presented my work, held at Imperial Collage London.

CCP5 2022

5th to 9th of September 2022

Presented a poster at the Theory-focused conference at the University of Huddersfield

British Carbon Group AGM 23

1st of March 2023

Presented a poster and won the best poster prize at the Royal Society London

PGR Science Showcase Poster Session 23

2nd of March 2023

Presented a poster at the science showcase held by TUOS.

Student Sustainability Research Conference 23

28th of March 2023 At the University of Leeds

Faraday Joint Conference 2023

3rd to 5th of April 2023 At the University of Sheffield

ANUMOCP 23

4th of July 2023 Presented my work, held at the University of York

Third year PhD talks at TUOS

5th of July 2023 Presented my work

Nanotech23

29th of August to 1st of September 2023 Presented my work at Brighton, University of Sussex

Publications

Paper:

Auty, A. J., Negar Mansouriboroujeni, Nagaraja, T., Dimitri Chekulaev, Sorensen, C. M., Das, S. R., Martsinovich, N., & Adrien. (2022). Ultrafast Transient Absorption Spectroscopy of Inkjet-Printed Graphene and Aerosol Gel Graphene Films: Effect of Oxygen and Morphology on Carrier Relaxation Dynamics. The Journal of Physical Chemistry C, 126(18), 7949–7955. https://doi.org/10.1021/acs.jpcc.2c01086

1. Introduction

CONTENTS

List of Figures		
Abbreviatio	ns	6
Overview		7
Graphen	e-Based Sensors for Real-Time Soil Analysis	7
1.1. Sma	rt Farming	8
1.1.1.	What is Smart Farming?	8
1.1.2.	Essential Nutrients in the Soil	9
1.1.3.	Sensors for Soil Monitoring	9
1.2. Sign	als in the soil	10
1.2.1.	SitS Motivation	10
1.2.2.	SitS Overview	10
1.2.3.	SitS Project Methodology	11
1.2.4.	Limitations and Possibilities	11
1.2.5.	PhD Project Purpose	11
1.3. Gra	phene	12
1.3.1. Ca	rbon Allotropes and Discovery of Graphene	12
1.3.2. Str	ucture and Key Properties of Graphene	13
1.3.2.1	. Carbon Hybridisation and atomic orbitals	13
1.3.2.2	2. Atomic Structure of Graphene	14
1.3.2.3	B. The Reciprocal Lattice of Graphene	15
1.3.2.5. Key Properties of Graphene16		
Ban	d Theory of Graphene	16
The Band Structure of Graphene18		
Che	mical Properties of Graphene	19
1.3.5. Me	ethods for Graphene Synthesis	19
1.3.5.1	. Top-Down Approaches	20
Med	hanical Exfoliation	20
Liqu	id-Phase Exfoliation	20
Che	mical Exfoliation or Reduction	20
1.3.5.2	2. Bottom-Up Approaches	20
Che	mical vapor deposition (CVD)	20
Epit	axial growth	21
The	unzipping of carbon nanotubes	21
1.3.5.3	8. Synthesis of Graphene and Graphene Aerogel Materials	21
1.3.6. Ap	plications	21
1.3.6.1	. Graphene as an Electrode	22

1.3.6.	2. Energy Storage	22
1.3.6.	3. Graphene in Smart Farming Applications	22
Bio	compatibility Issues of Graphene in Agriculture	22
Ob	stacles and Limitations for Applications of Graphene in Agriculture	23
1.4. Gra	aphene Oxide	24
1.4.1.	Overview of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)	24
1.4.2.	Synthesis of GO and rGO	24
1.4.3.	Properties	25
1.4.4.	Applications	25
1.5. Gra	aphene Nanoribbons	27
1.5.1.	Synthesis	27
1.5.2.	Properties of nanoribbons	27
1.6. Gra	aphene with Defects	29
1.6.1.	Stone–Wales defects	29
1.6.2.	Single vacancy defects	29
1.6.3.	Multiple vacancy defects.	29
1.6.4.	Oxygen substitution	
1.7. Gra	aphene Aerogels	
1.7.1.	Structure and Properties	31
1.7.2.	Synthesis	
Hydro	othermal reduction	
Chem	ical reduction	
Cross	-linking methods such as Hydrogen bonds	
Printi	ng of Graphene Aerogels	
Dir	ect Ink Writing (DIW)	
Ste	reolithography (SLA)	
1.7.3.	Applications and Potential	
1.8. Na	notubes	
1.8.1.	Structure of Carbon Nanotubes:	
1.8.1.	1. Zigzag Nanotubes	
1.8.1.	2. Armchair Nanotubes	
1.8.1.	3. Chiral Nanotubes	
1.8.2.	Properties	
1.8.3.	Applications of CNTs	34
1.9. Ser	nsors	35
1.9.1.	Phosphate Sensors	

1.9.2.	Graphene-Based Sensors	
1.10.	Research Aims	
1.10.1.	PhD Project Aim:	
1.10.2.	Research Techniques	
Expe	erimental Techniques	
Theo	pretical Methods	
1.11.	References	

LIST OF FIGURES

Figure 1.1. Signals in the Soils image, taken from NSF-USDA-UKRI Virtual SitS workshop – Principal Investigators Workshop – Dr Suprem Das (Kansas State University)

Figure 1.2. Some Allotropes of Carbon- This figure depicts the structure of diamond, the structures of graphite and single-layer graphene, a C60 buckyball, an amorphous carbon, a nanocone, a chiral carbon nanotube, and lonsdaleite - drawn using 'Avogadro'.

Figure 1.3. The Hybridisation of Carbon in Ground State and Hybridised States

Figure 1.4. The sp2 Hybridisation in Graphene.

Figure 1.5. The structure of graphene (a) Bravais lattice; (b) reciprocal lattice

Figure 1.6. A Schematic Figure of the Valence (V) and Conduction (C) Bands of Metals, Semiconductors and Insulators.

Figure 1.7. Comparison between a 'volumetric plot' and a 'band structure plot' of graphene

Figure 1.8. The Density of States of Graphene calculated using SIESTA and plotted using OriginPro.

Figure 1.9. Representative Chemical Structures of (a) Reduced Graphene Oxide and (b) Graphene Oxide, Drawn Using Avogadro Software.¹⁹

Figure 1.11. Point Defects in Graphene: (a) Vacancy, (b) Stone-Wales (5775) defect, (c) Oxygen Substitution

Figure 1.12. Single-Walled Carbon Nanotubes (a) Zigzag (b) Armchair (c) Chiral.

Figure 1.10. Structures of Graphene Nanoribbons (GNRs) are Shown: (a) Armchair GNR and (b) Zigzag GNR.

ABBREVIATIONS

BLG	Bilayer Graphene
CNT	Carbon Nanotube
CVD	Chemical vapour deposition
DFT	Density Functional Theory
DIW	Direct Ink Writing
DOS	Density of States
DV	Double Vacancy
GA	Graphene Aerogel
GNR	Graphene Nanoribbon
GO	Graphene Oxide
GPS	Global Positioning System
юТ	Internet of Things
LPE	Liquid Phase Exfoliation
MAG	Micro Architected Graphene
MIPs	Molecularly Imprinted Polymers
MWCNTs	Multi-Walled Carbon Nanotubes
Р	Phosphate
rGO	Reduced Graphene Oxide
SitS	Signals in the Soil
SLA	Stereolithography
SLG	Single Layer Graphene
SV	Single Vacancy
SWCNTs	Single-Walled Carbon Nanotube
XGO	Crosslinked Graphene Oxide

Introduction

OVERVIEW

Graphene-Based Sensors for Real-Time Soil Analysis

The Signals in the Soils (SITS)¹ project is a collaboration between UK and US universities which aims to develop affordable, selective sensors for detecting soil phosphates by utilising graphene's unique properties as a sensor material. This project intends to enhance the monitoring of soil nutrient levels by concentrating on phosphates, an essential plant nutrient. The sensor technology holds the potential to transform the analysis and monitoring of soil health, thereby promoting more sustainable and environmentally friendly agricultural practices. These sensors will enable farmers to optimise the use of fertilisers, resulting in minimised waste, reduced water contamination, and a lower environmental impact.

My doctoral research project employs ultrafast spectroscopy and computational tools to investigate the potential of graphene and its derivatives as materials for advanced electrochemical sensors designed for phosphate detection. Graphene's unique characteristics, such as its high surface area and adjustable electronic structure, position it as a promising candidate for sensor technology advancement. This PhD project showed that functionalised graphene with as little as 3% oxygen content can exhibit an open band gap, transforming it into a semiconductor suitable for sensor applications.

1.1. SMART FARMING

1.1.1. What is Smart Farming?

According to the United Nations, the global population is projected to reach 9.7 billion by 2050 and a staggering 11 billion by 2100,² necessitating a substantial increase in food production. However, resource scarcity due to climate change and urbanisation further complicates the challenge, underscoring the urgent need for innovative solutions in the field of agriculture.

Recent analyses have emphasised the imperative for enhanced and sustainable food production in order to cater to the needs of the global population. The correlation between population growth and food security is complex and multifaceted. It is also argued by some that current production levels are sufficient. However, it is vital to optimise distribution and minimise food waste in order to ensure fair access to the available food resources. Addressing these challenges demands a multi-pronged approach that encompasses the entire food supply chain.³

The evolution of agriculture from traditional to smart farming has been made possible by implementing advanced technologies. In ancient times, agriculture was a means of survival, with humans cultivating the land using basic but essential tools. This era, known as 'Agriculture 1.0', gave way to 'Agriculture 2.0' in the 20th century. 'Agriculture 2.0' focused on increased productivity and reduced labour costs through mechanisation. This era saw the introduction of machinery for harvesting, weeding, irrigation, sowing, and seed preparation. Farmers transitioned from manual labour to machines, leading to increased reliance on fossil fuels like gas and oil. Advancements in transportation also played a crucial role in establishing efficient food supply chains.⁴

'Agriculture 3.0', which spanned from the late 20th to the early 21st century, introduced precision farming and data-driven decision-making. Communication technologies, software engineering, and the Internet of Things (IoT) were integrated with farm equipment during this era. Furthermore, farmers embraced renewable energy sources such as hydropower, solar photovoltaic, and wind power. They also adopted innovative and smart farming technologies such as crop prediction and recommendation, variable rate applications, optimising inputs based on field conditions, yield monitoring, and knowledge systems for farmers. 'Agriculture 3.0' represented a significant shift from purely mechanical techniques to a more data-driven approach.⁴

Finally, 'Agriculture 4.0' emerged, focused on organic farming and utilising modern science to enhance agricultural activities. This fourth generation in the evolution of agriculture revolutionised the smart farming industry by incorporating specific technologies that cater to consumer needs or specific environmental needs. Thanks to novel scientific expertise, farmers have begun to improve agricultural practices sustainably through intelligent farming.⁴

Smart farming also referred to as precision agriculture, is a sophisticated and continually progressing methodology that employs cutting-edge techniques and data-driven analyses to enhance crop production and resource allocation and management. Its overarching objective is to move away from traditional, 'one-size-fits-all' farming practices and instead make informed decisions based on precise data that caters to the specific needs of each field, crop, and individual plant. Smart farming offers unparalleled precision and efficiency in modern agriculture by leveraging innovative techniques such as precision planting, variable rate irrigation, and real-time crop monitoring.⁴

This revolutionary approach to farming promises significant benefits to farmers and the environment. One of the primary benefits is the ability to achieve higher crop yields by smartly managing resources and applying targeted interventions. By minimising waste and optimising resource usage, such as fertilisers, farmers can save money on costs. Additionally, precision agriculture helps reduce chemical and water usage, leading to improved environmental sustainability and resource conservation. Farmers can also make informed decisions about their land and crops by leveraging data-driven insights, leading to better outcomes. One of the applications of precision agriculture is using sensors to collect data on various field aspects, such as soil moisture, nutrient levels, temperature, and pest activity. Analysing this information with specialised software and algorithms can identify patterns, trends, and potential issues. This allows farmers to adjust inputs, such as fertiliser, in a highly precise manner tailored to the specific needs of each area within a field, promoting sustainability and efficiency.⁵ Precision irrigation systems are also employed to deliver water precisely to the areas and times when it is needed, thus minimising water waste and alleviating crop stress.⁶ To further enhance efficiency, advanced machinery equipped with sensors and GPS can navigate fields autonomously, performing tasks like planting and harvesting with greater accuracy.⁷

1.1.2. Essential Nutrients in the Soil

Certain essential nutrients, such as phosphorus and nitrogen, are critical for soil health and plant growth. They play a vital role in the soil-plant system and have a direct impact on crop production and yield. Specifically, phosphates (P) are required for various plant functions, including energy transfer, photosynthesis, and root development.⁸ Inadequate phosphorus levels in the soil can lead to reduced crop yields and have adverse effects on the sustainability of agricultural practices. Overreliance on outdated methods for estimating phosphorus needs leads to inefficient or excessive fertiliser use.⁹

Measuring P levels accurately in the soil is crucial to optimise fertiliser application and ensure optimal crop growth. However, traditional methods for P analysis are time-consuming and expensive, delaying farmers' timely decision-making. Recent research has highlighted the importance and benefits of real-time portable phosphorus and nitrogen monitoring devices, such as a chip-level colourimeter.¹⁰ This method allows farmers to promptly assess their fertiliser utilisation on their premises, enabling them to make well-informed decisions that lead to reduced costs and minimised environmental impact. Highly sensitive sensors are also being used and studied currently for real-time nutrient monitoring, which will help impact sustainable agriculture that has the potential to benefit future generations.⁹

1.1.3. Sensors for Soil Monitoring

Smart farming uses modern technology, equipment, and devices such as sensors, GPS, robots, and aerial imagery; it requires the integration of techniques such as real-time data collection. Rapid developments in machine learning techniques and sensor technologies have been found to be a cost-effective solution in smart agriculture. Sensors are being used in smart agriculture to measure the status of plant leaves and soil as part of the fusion of information technologies that transform digital farming.¹¹

Recent advancements in research have led to the development of imaging technologies and plant biomarkers for intelligent fertiliser management, aiming to improve the efficiency of fertiliser usage and promote sustainability within the agricultural sector. Excessive fertilisation can have adverse effects on the environment and lead to resource wastage, underscoring the importance of precise fertiliser application. The adoption of smart fertiliser management, which integrates data, sensors, and imaging techniques, offers a viable solution for optimizing fertilizer application.¹²

Challenges include developing efficient and affordable biomarker sampling and analysis methods, integrating various data sources for comprehensive nutrient management, and validating and implementing these technologies in field conditions for different crops and soil types. Quantitative nutrient biomarkers may allow for precise measurements of nutrients. Smart fertiliser management has the potential to enhance crop yield and make more efficient use of resources.¹³

Examples discussed in this section show the important growing role of advanced technologies in agriculture, such as sensors for monitoring nutrients. The development of such technologies relies on advances in physics, chemistry, and materials science; for example, developing new sensor devices requires an in-depth understanding of the properties of materials used in these devices. This serves as the motivation for the Signal in the Soil (SitS) project, which this PhD project is part of.

1.2. SIGNALS IN THE SOIL

1.2.1. SitS Motivation

Signals in the Soils (SitS), a collaborative research program funded by the National Science Foundation (NSF) and NERC, brought together universities from the United States and the United Kingdom to develop technological solutions for agriculture. This interdisciplinary project, titled "Real-time and Continuous Monitoring of Phosphates in the Soil with Graphene-Based Printed Sensor Arrays", aims to develop a low-cost, in-situ, real-time sensor for monitoring soil phosphate levels. To achieve this, the development process was divided into several work packages. The first work package focused on optimising and characterising graphene material for the sensor. Other work packages addressed designing the sensor itself, validating its suitability for real-world soil application, and designing the wireless data transfer setup to enable real-time monitoring capabilities.

Combining expertise in engineering, agriculture, environmental science, and materials chemistry, SitS has the potential to significantly impact sustainable food production, fertiliser use regulation, economic security, and technological advancement. The SitS project aimed to facilitate interdisciplinary collaboration between the fields of science, technology, agriculture, and environmental science. This was achieved through the training of graduate students, undergraduate students, and postdoctoral scientists.

1.2.2. SitS Overview

The US teams worked on developing and producing printable graphene aerosol gels as the sensor material, conducting soil analysis, and developing wireless sensor technology. To complement this, the UK team studied the electronic properties of this novel printable graphene material using laser spectroscopy and computational modelling. The project aimed to develop a real-time phosphate sensor using printable graphene inks by integrating all aspects of sensor research, from fundamental physical properties of sensor materials to field testing and wireless data transmission.



Figure 1.1. Signals in the Soils image, taken from NSF-USDA-UKRI Virtual SitS workshop – Principal Investigators Workshop – Dr Suprem Das (Kansas State University)

The sensor technology has been designed to be portable and will be seamlessly integrated with a wireless system for continual in-field monitoring. This integrated system will enable the real-time transmission of electrochemical signals, allowing for the immediate mapping of soil phosphate levels

across varied agricultural terrains. The initial roll-out was scheduled for deployment in the US Midwest (specifically Kansas) and the UK East Midlands (including Derbyshire Dales and Peak District).

1.2.3. SitS Project Methodology

The core of the research methodology involved developing sensor arrays using 3D printing, also known as additive manufacturing, with tailored graphene materials. These materials were optimized for both high conductivity and efficient phosphate detection. Early research in the project, led by Dr. Suprem Das, demonstrated that graphene aerogel (GA)-based sensors exhibited superior performance compared to sensors made from pure graphene. This finding, while not yet published, significantly influenced the direction of the project. To further enhance phosphate detection, chemically functionalized GA and other graphene-based materials were explored. The project utilized ultrafast laser spectroscopy and computational modelling to understand the electronic properties of these materials and their interactions with phosphates. Finally, controlled environment testing in Kansas, the US, and the UK was set to take place to investigate sensor performance in various soil types, though initial field testing was limited due to time constraints.

1.2.4. Limitations and Possibilities

Using graphene-based sensors to test soil is technically feasible; however, it is the key technical challenge of the project, and questions remain regarding their cost-effectiveness, scalability, durability, and lifespan. Although one of the main aims of this SitS project is to create inexpensive sensors, it is unclear how much cheaper they are compared to existing soil testing methods. Additional investigation and research are necessary to estimate the production costs and to determine whether the sensor arrays can be manufactured and produced at a low cost for widespread adoption in agriculture. Besides this, the durability and lifespan of the sensors in field conditions need to be evaluated to ensure their effectiveness over time.

Regarding practical applications, data transfer and user interface are two essential factors to consider. Agricultural farmers need to be able to easily and quickly access and interpret the sensor data to make informed decisions about fertiliser usage. Therefore, establishing efficient data transfer methods and providing a user-friendly interface is crucial. Additionally, it is vital to ensure that the sensors are compatible with existing farming practices. It could hinder their adoption if the sensors require significant changes to current agricultural workflows.

The sensor technology is expected to have a long-term impact on agricultural practice, particularly the potential reduction in fertiliser use and water pollution resulting from precise phosphorus monitoring. These benefits could have significant environmental advantages, and it is essential to quantify them in the long run. Additionally, assessing the economic impact of the research, such as increased crop yields and improved farmer profitability, is equally important. An immediate next step is to explore broader applicability of the sensor technology to monitor other essential soil nutrients and environmental parameters.

1.2.5. PhD Project Purpose

This PhD project was a fundamental part of the SitS program and focused on studying graphene materials for use in sensor devices. The aim was to investigate the electronic and optical properties of graphene materials that were synthesised at Kansas State University and used in the sensors to understand the relationship between these materials' structure and properties. The study utilised ultrafast laser spectroscopy at the University of Sheffield and various other characterisation techniques to investigate novel graphene-based materials' electronic and charge carrier dynamic properties. Computational modelling was also used to explore various graphene morphologies and chemical modifications and to identify the effects of oxygen functional groups and curvature on graphene's electronic and optical properties.

1.3. GRAPHENE

1.3.1. Carbon Allotropes and Discovery of Graphene

To understand the atomic structure of graphene, it is helpful first to understand the atomic structure of elemental carbon and its 2D and 3D allotropes.¹⁴ Carbon exhibits an interesting ability to form unique structures by bonding in different ways (Figure 1.2). What makes these structures intriguing is the varied hybridisations that carbon atoms can adopt. In particular, when four valence electrons have equal energies, sp³ hybridised orbitals are formed, as discussed in more detail in the next section. Bonding of these sp³ carbons produces an isotopically strong diamond. Conversely, if only three electrons per carbon atom form covalent bonds in a plane, while the fourth electron delocalises above the plane of atoms, the resulting material is graphite. This sp² hybridisation builds a layered structure with strong in-plane bonds and weak out-of-plane van der Waals bonding. Graphite is a 'soft' material due to its ability to slide along the planes.¹⁵ In 1985, a research team led by Smalley, Kroto, and colleagues discovered a novel form of carbon known as buckminsterfullerene C₆₀, shown in Figure 1.1.¹⁶ This molecule resembles a 'football' and is composed of pure carbon atoms bonded in hexagon and pentagon rings of sp²-bonded carbons. The discovery of C₆₀ was so significant that it earned the Nobel Prize in Chemistry in 1996.¹⁷

Graphite is an allotrope of carbon that conducts electricity and is used in various applications. Unlike diamonds, graphite is a semimetal.¹⁵ Novoselov and Geim from the University of Manchester made a groundbreaking discovery in 2004. They found that by using the Scotch Tape method, they could obtain graphite nanosheets that were only a few atoms thick, including single-layer graphene, which was an astonishing 0.335 nanometres thin. The method involved carefully polishing the surface of the graphite to remove incomplete layers and impurities. The researchers were surprised to find that the by-products on the tape were graphene, which they later studied and characterised. The researchers' goal was to explore the electronic properties of these materials to create innovative devices.¹⁸



Figure 1.2. Some Allotropes of Carbon- This figure depicts the structure of diamond, the structures of graphite and single-layer graphene, a C₆₀ buckyball, an amorphous carbon, a nanocone, a chiral carbon nanotube, and lonsdaleite - drawn using 'Avogadro'.¹⁹

Graphene is an exceptional nanomaterial that combines a simple atomic structure with intriguingly intricate physics. It is a single layer of carbon atoms arranged in a honeycomb lattice pattern, creating densely packed six-membered rings. With its unique properties, graphene is a cornerstone for diverse carbon-based nanomaterials. All the carbon atoms in graphene are sp² hybridised, making it an excellent conductor of heat and electricity.¹⁵ Graphene is optically transparent but structurally dense, impermeable even to gases.²⁰ After its initial isolation, researchers have explored numerous potential applications for graphene, such as flexible electronics, supercapacitors or energy storage devices.^{21,22}

In particular, graphene that has been appropriately modified to exhibit semiconducting properties is considered a promising candidate for replacing silicon in electronic devices.²³ The discovery of graphene led to the discovery of other graphene-based nanomaterials.¹⁵

Graphene's exceptional electronic properties, including its high electrical conductivity, coherent electron transport, tuneability, and exceptional mechanical strength and stability, have captured the attention of scientists and technologists alike. Mono-layer graphene possesses three electronic properties that have ignited interest in this material. These include the disappearance of carrier density at the Dirac points, pseudo-spin presence, and carriers' relativistic behaviour.¹⁴

Besides the most well-known forms of carbon, such as graphene and diamond, there are also other interesting allotropes of carbon, such as lonsdaleite, amorphous or porous carbon, and carbon-based nanomaterials, such as nanotubes, nanoribbons, nanocones, and nanothreads.²⁴ Some of these structures are shown in Figure 1.2.

1.3.2. Structure and Key Properties of Graphene

1.3.2.1. Carbon Hybridisation and atomic orbitals

Carbon, a tetravalent element, has the atomic number 6, and at its ground state, its electrons can occupy the 1s, 2s, and any two 2p^o orbitals as depicted in Figure 1.3. Only the four outermost electrons of a carbon atom participate in the bond formation.¹⁴



Figure 1.3. The Hybridisation of Carbon in Ground State and Hybridised States

A carbon atom can undergo sp³ hybridisation, wherein one 2s electron is promoted to the vacant 2p orbital. This intermixing of one 2s and three 2p orbitals from the same shell generates four sp³ hybrid orbitals with equivalent energies and a tetrahedral arrangement. Consequently, the carbon atom can form four covalent bonds, and the resulting molecular geometry exhibits bond angles of approximately 109.5°.¹⁴ Carbon can adopt sp hybridisation, when one 2s and one 2p orbital are hybridised, forming two double bonds or one single and one triple bond, resulting in linear molecules with 180° bond angles. In the context of trivalent bonding relevant to graphene, a carbon atom

exhibits sp² hybridisation (Figure 1.3). This involves the hybridisation of one 2s orbital with two 2p orbitals, forming three trigonally arranged planar sp² hybrid orbitals, and leaving one unhybridised 2p orbital. These orbitals form two σ bonds and one π bond with three neighbouring atoms, resulting in a triangular arrangement with bond angles of approximately 120°.¹⁴

1.3.2.2. Atomic Structure of Graphene

The sp² hybridisation of carbon atoms in Graphene results in a trigonal planar arrangement, as shown in Figure 1.4. This hybridisation forms strong σ -bonds within the plane, contributing significantly to graphene's structural robustness. Unique to graphene, these hybridised orbitals leave behind unhybridised p-orbitals perpendicular to the plane. These p-orbitals form π -bonds, generating a halffilled π -band responsible for graphene's electronic properties.



Figure 1.4. The sp² Hybridisation in Graphene.

The in-plane covalent bonds cause the graphite and graphene's 'honeycomb' structure, resulting in a two-dimensional lattice. The electrons in the unhybridised 2p orbitals are delocalised. The delocalisation of electrons in a monolayer graphene sheet is shown in Figure 1.4, indicating that carbon atoms have a bond order of approximately 1.33 because of the delocalisation of the π - electrons; each atom forms three σ bonds and one π bond. Within graphene layers, in-plane bonds surpass the strength of C-C bonds in sp³-hybridized diamond (615 kJ/mol vs. 345 kJ/mol). As predicted by Hearing in 1958, graphite possesses a lattice constant of a = $\sqrt{3} a_0$, where $a_0 \approx 1.42$ Å represents the nearest-neighbour interatomic distance.¹⁴



Figure 1.5. The structure of graphene (a) Bravais lattice; (b) reciprocal lattice²⁵

The term "graphene" specifically refers to a single, isolated monolayer of carbon atoms arranged in a hexagonal lattice, which was first isolated by Novoselov in 2005. While electrons can flow effortlessly

in the graphene structure, leading to intriguing electrical properties, the electronic properties of fewlayer graphene are highly dependent on the number of constituent layers. Only single-layer graphene (SLG) exhibits true zero-gap semiconductivity. Bilayer graphene (BLG), however, has a small band gap due to the bending of the conduction and valence bands near graphene's Dirac point. Conversely, "few-layer graphene" (FLG, comprising 3 to <10 layers) experiences band overlap, leading to the emergence of multiple charge carriers. Graphene structures exceeding this thickness are more appropriately classified as thin graphite films.¹⁴

Graphene does not have a 'true' Bravais lattice; instead, it is made up of two triangular Bravais lattices, shown using blue dashed triangles in Figure 1.5(a). The Bravais lattice or the direct lattice, is a periodic array of points (atoms) connected with lattice vectors. Lattice vectors describe the direct lattice:

$$R = t\boldsymbol{a} + u\boldsymbol{b} + v\boldsymbol{c} \tag{1.1}$$

where *t*, *u*, *v*= integers and *a*, *b*, *c* = lattice vectors

The volume of the unit cell V is given by:

$$V = \mathbf{a} \cdot (\mathbf{b} \times \mathbf{c}) = \mathbf{b} \cdot (\mathbf{c} \times \mathbf{a}) = \mathbf{c} \cdot (\mathbf{a} \times \mathbf{b})$$
(1.2)

The hexagonal graphene lattice's unit cell comprises two atoms separated by a distance of 1.42 Å.²⁶ The graphene lattice can also be described as two intermingled triangular sub-lattices; this is pictured in Figure 1.5(a) with black and white circles representing carbon atoms belonging to the two sub-lattices; the sub-lattices are also commonly denoted A and B, where three B sub-lattice atoms surround each atom on the A sub-lattice and vice versa.

1.3.2.3. The Reciprocal Lattice of Graphene

The reciprocal lattice of graphene is a discrete set of points in reciprocal space that correspond to the periodicity of the real-space lattice. In simpler terms, each point in the reciprocal lattice generates a plane wave that perfectly diffracts from the periodic arrangement of atoms in graphene.²⁷

The hexagonal Brillouin zone (BZ) of graphene is the primitive cell of the reciprocal lattice and is the hub of electronic state information for this material. The Dirac points, which are at the boundaries of the BZ, are pivotal to graphene's electronic behaviour, giving rise to its exceptional traits such as high carrier mobility and Klein tunnelling. By comprehending the reciprocal lattice, we can examine electron diffraction patterns, calculate phonon dispersion curves, and delve into other significant physical phenomena in graphene.²⁷ The reciprocal lattice in Figure 1.5(b) is used to describe the electronic properties of graphene. The reciprocal lattice is the Fourier transform of another lattice (direct lattice). The concept of the reciprocal lattice was proposed by Leon Brillouin (1889–1969).²⁸

The reciprocal lattice is valuable for visualising graphene's electronic band structure by plotting the bands along specific directions within the Brillouin zone. For instance, graphene bands are usually plotted along paths connecting Γ (origin) to M or K points. Notably, the K and K' points (Dirac points) hold particular significance due to their unique properties. Their coordinates in reciprocal space can be expressed below, where a represents the direct lattice constant.

$$K = \begin{pmatrix} 2\pi/\sqrt{3a} \\ 2\pi/3a \end{pmatrix} \text{ and } K' = \begin{pmatrix} 2\pi/\sqrt{3a} \\ -2\pi/3a \end{pmatrix}$$
(1.3)

In a reciprocal lattice, the basis vectors of the reciprocal lattice a^* , b^* and c^* are defied as:

$$\boldsymbol{a}^* = 2\pi \frac{(\boldsymbol{b} \times \boldsymbol{c})}{V} \quad \boldsymbol{b}^* = 2\pi \frac{(\boldsymbol{c} \times \boldsymbol{a})}{V} \quad \boldsymbol{c}^* = 2\pi \frac{(\boldsymbol{a} \times \boldsymbol{b})}{V}$$
(1.4)

Where,

$$V = \boldsymbol{c} \cdot (\boldsymbol{a} \times \boldsymbol{b}) \tag{1.5}$$

The reciprocal lattice is:

$$K_i = h\boldsymbol{a}^* + k\boldsymbol{b}^* + l\boldsymbol{c}^* \tag{1.6}$$

where h, k, l = integers, a, b, c = lattice vectors, a^*, b^*, c^* - reciprocal lattice vectors defined in equation (1.4). (This only applies to a rectangular lattice).

The 2D hexagonal unit cell of graphene contains two carbon atoms. The valence atomic orbitals involved in the carbon atoms are the 2s, 2px, 2py, and 2pz orbitals. Therefore, in tight-binding models, the band structure of the graphene unit cell (excluding core orbitals) typically considers eight bands. However, it is important to note that there are potentially further unoccupied bands, as electrons can be promoted to higher orbitals like 3s, 3p, etc. The 2pz orbitals are orthogonal to the sp² orbitals at all points of the Brillouin zone. This gives two π bands and six σ bands. At the Γ (gamma) point, the 2s orbital does not mix by symmetry with C 2px and 2py; sigma sub 1 (σ_1) is purely C 2s bonding at Γ , while sigma sub 2 (σ_2) and sigma sub 3 (σ_3) are antibonding 2p at Γ . σ_1 , σ_2 , σ_3 represent distinct subtypes of sigma bonds formed at the Γ point. σ_1 arises from direct 2s orbital overlap, leading to the strongest σ bonds. In contrast, σ_2 and σ_3 stem from antibonding interactions of 2p orbitals, resulting in weaker σ bonds compared to σ_1 .^{25,28}

1.3.2.5. Key Properties of Graphene

Band Theory of Graphene

Band theory is a key concept in condensed matter physics that explains the organization of electronic energy levels in materials like graphene. It helps classify materials as conductors, insulators, or semiconductors and reveals how electronic configurations and bonding strengths relate to conductive properties.

Band theory describes the electron energies in solids through energy bands. The Fermi level indicates the chemical potential of electrons in semiconductors, typically positioned within the band gap between the occupied valence band and the unoccupied conduction band. This location is crucial for electrical conductivity. By doping, the Fermi level can be adjusted to create n-type semiconductors with electrons as charge carriers or p-type materials with holes that conduct electricity. Band theory allows us to predict and engineer the electrical properties of semiconductors, and a nearest neighbour tight-binding calculation can estimate the band structure of monolayer graphene.²⁷

The two most chemically important energy bands that determine the chemical and electronic properties of solids are the valence band and the conduction band (Figure 1.6). The valence band, the highest-filled band containing electrons responsible for bonding between atoms, consists of the highest energy orbitals occupied by electrons. In contrast, the conduction band, the empty band above the valence band where electrons are free to move and contribute to electrical conductivity, comprises the lowest unoccupied orbitals. The band gap is the region that separates these two bands. The Fermi level is located exactly in the middle of this gap for undoped defect-free semiconductors. In contrast, in graphene, which is a zero-gap semiconductor, the Fermi level lies at the merging point of the valence and conduction bands.

The density of states measures the number of electronic states available at each energy level within the material. This distribution determines the fundamental electronic properties of graphene, which is known for its distinctive behaviour. In graphene, the density of states at the Fermi level is zero.



Figure 1.6. A Schematic Figure of the Valence (V) and Conduction (C) Bands of Metals, Semiconductors and Insulators.

The width of a material's band gap influences its electrical conductivity. Materials with wide gaps are insulators, while those with narrow gaps are semiconductors, and overlapping bands indicate conductors. In semiconductors, doping creates additional energy levels in the forbidden gap, impacting conductivity. Understanding energy bands is crucial in electronics, materials science, and photovoltaic devices.

Insulators have a wide band gap, typically 3 electron volts or more, that separates the valence and conduction bands, requiring significant energy for electrons to be excited into the conduction band. This results in minimal electrical conductivity due to the lack of free electrons. In contrast, metals feature overlapping or closely situated valence and conduction bands, allowing electrons from the filled valence band to easily move into the conduction band. This availability of free mobile charge carriers leads to high electrical conductivity in metals. Compared to insulators (Figure 1.6), semiconductors possess a smaller band gap, typically between 1-3 electron volts. This allows for the excitation of electrons from the valence band to the conduction band through thermal energy or light absorption, ultimately creating mobile charge carriers - electrons in the conduction band and holes in the valence band. Introducing impurities through doping increases the number of charge carriers, allowing for control of the semiconductor's conductivity.

Unlike regular conductor or semiconductor materials, graphene has a distinct electronic band structure due to being a single-layered material made up of carbon atoms. While conventional semiconductors have a clear gap between the valence and conduction bands, graphene has a zero band gap. This means that the valence and conduction bands intersect at specific points in the Brillouin zone, known as Dirac points. The energy bands disperse linearly with momentum near the Dirac points, forming Dirac cones. This linear dispersion results in massless charge carriers, which behave like relativistic particles described by the Dirac equation.²⁹ The electronic band structure of graphene can be effectively described using the tight-binding model.²⁷ This model considers the interaction between electrons on neighbouring carbon atoms, forming bonding and anti-bonding states. In graphene, the bonding and anti-bonding π -orbitals of carbon atoms touch, resulting in the characteristic Dirac cones.

Electrons in graphene are described as chiral a result of its honeycomb lattice structure. This distinctive attribute is due to the need for two-component wavefunctions for its quasiparticles, which is influenced by the sublattices A and B within the honeycomb lattice. In graphene, this sublattice dependence is known as "pseudospin" (σ). Chirality is a property related to the pseudospin and the direction of motion of an electron. It's positive for electrons and negative for holes, and it helps unify the description of these particles in graphene. In addition, the Dirac points in graphene exhibit valley degeneracy, meaning there are two distinct valleys in the Brillouin zone with identical electronic

properties but opposite chirality due to their sublattice origin. Depending on their spin direction, these electrons have different effective velocities, leading to intriguing phenomena like the anomalous Hall effect.³⁰

Graphene's honeycomb lattice structure results in a linear dispersion relation near the Fermi level, leading to its semi-metallic nature with exceptional electron mobility.³¹ The dispersion relation exhibits Dirac cones, resulting in distinctive electronic properties such as Klein tunnelling and half-integer quantum Hall effect.²⁷ By introducing defects, and functionalisation like adding epoxides, doping the material, or inducing defects, the band gap of graphene can be opened, enabling its use in various electronic devices like photodetectors and sensors.³²

The Band Structure of Graphene

At the Γ point, the π band is entirely bonding, and the π^* band is antibonding, with the maximum separation between the two bands. Figure 1.7 illustrates the band structure of graphene. At M, the π band is weakly bonding, and the π^* band is weakly antibonding. Each carbon forms one π bonding and one π^* antibonding orbital. At K the π and the π^* bands are both nonbonding and become degenerate so that the bands come into contact with each other, causing graphene to act as a semimetal. At K, the phase of the orbitals changes once every three-unit cells. The π bands are associated with the valence band, and the π^* bands are associated with the conduction band. The valence and the electron energy. As mentioned, the valence and the conduction band meet at exactly the Fermi energy level.

The 3D plot of the 2D band structure of graphene in Figure 1.7 show that at the high symmetry K' and K points the π and the π^* bands (the valence and conduction bands) touch and become degenerate. These points are called the Dirac points. In intrinsic graphene, each carbon atom contributes one electron to the π band, completely filling the valence band and leaving the conduction band empty. The Fermi level is situated precisely at the energy where the conduction and valence bands meet (Dirac point), which is also referred to as the charge neutrality points.



Figure 1.7. Comparison between a 'volumetric plot' and a 'band structure plot' of graphene ³³

Moving away from the Dirac points (K), the energies on the π and π^* band change linearly with the k vector. Looking at the 3D band structure plot, it is shown that graphene possesses a band gap of exactly zero, and the density of states for graphene is also zero at this point. Due to its twodimensional lattice structure, electrons in graphene primarily have momentum in two directions. Consequently, the Dirac points can be more precisely described as forming a Dirac cone, as illustrated in Figure 1.7.



Figure 1.8. The Density of States of Graphene calculated using SIESTA³⁴ and plotted using OriginPro.³⁵

Figure 1.8 shows the density of states of graphene computed using density functional theory. This illustrates that the density of states (DOS) is zero at the Dirac point (at the energy of 0 eV), but there is no energy gap between the valence and conduction bands.

Chemical Properties of Graphene

Graphene is a material that has many exceptional physical and chemical properties. It is a conductor of electricity with a remarkably high electron mobility, making it an excellent choice for electronic applications. In addition, graphene exhibits exceptional heat conductivity, making it a suitable option for thermal management. It is exceptionally robust and has a high tensile strength, making it an ideal candidate for structural applications. Graphene is almost entirely translucent, allowing use in transparent conductive materials. Also, it is impervious to gases and liquids, making it a compelling option for various barrier applications. Graphene is highly malleable and can be twisted and stretched without compromising its structural integrity. Finally, it is exceptionally lightweight, with low density.¹⁴

Graphene sheets can undergo chemical reactions at the edges or within the bulk lattice. The atoms at the sheet edges differ from those within the lattice because edge atoms lack neighbouring carbon atoms. Atoms within the bulk graphene lattice are chemically identical, forming a pure π -conjugated system. A graphene sheet becomes a polycyclic aromatic hydrocarbon when reduced to the molecular level. Functionalising the bulk graphene sheet can be achieved via covalent or non-covalent methods. Covalent functionalisation requires breaking C-C bonds and utilises a broad range of reactions. Non-covalent functionalisation relies on van der Waals forces, often due to π - π stacking between aromatic molecules and the graphene lattice, similar to how graphene sheets are held together in graphite.³⁶

By introducing functional groups, such as epoxides, doping the material, or inducing defects, the band gap of graphene can be opened, enabling its use in various electronic devices like photodetectors and sensors. Graphene can also be functionalized by adding hydroxyl and epoxide groups, forming graphene oxide and reduced graphene oxide. This is directly relevant to this thesis, which investigates oxygen-containing graphene, where oxygen is believed to be introduced during synthesis.³²

1.3.5. Methods for Graphene Synthesis

The synthesis of graphene is critical to its function in practical applications. The most straightforward and common way to produce graphene is through graphite exfoliation, although there are other methods for synthesising graphene.³⁷ Generally, two approaches exist for producing graphene: the top-down and the bottom-up approaches. The choice of technique depends on the desired quality and scale of production.

1.3.5.1. Top-Down Approaches

Top-down approaches involve beginning with bulk material such as graphite and then separating it into individual graphene sheets. While this method generally results in lower yields, it can yield higherquality graphene flakes, depending on the specific techniques employed.

Mechanical Exfoliation

This method involves peeling off graphene sheets from graphite using adhesive tape. It is a simple and reliable way to produce high-quality graphene, but the yield is very low, making it impractical for large-scale production. Geim and Novoselov used this method to prepare a single graphene sheet by peeling off a sheet of graphite using scotch tape.³⁸ This method, called the scotch tape approach, involves repeatedly peeling highly oriented pyrolytic graphite using scotch tape. The process has been optimised to produce single-layer graphene (SLG) with high structural quality and more than 100 μ m² in size.^{39,40} The mechanical exfoliation method is cost-effective and capable of generating high-quality single-layer graphene, although it is not feasible for large-scale graphene production due to limited scalability and the production of small flakes.

Liquid-Phase Exfoliation

Graphite is composed of 2D layers that are weakly stacked to form 3D structures. The process of exfoliating these layers results in nanosheets, effectively increasing the material's surface area. This enhancement positively impacts the material's chemical and physical reactivity, making it crucial for various applications, including catalytic materials, ion exchange, fillers in composites, and intumescent materials, which expand when exposed to heat. The liquid phase exfoliation (LPE) method involves dispersing graphite in a liquid solvent and then utilizing techniques such as sonication to break apart the layers. While this method can produce larger quantities of graphene compared to mechanical exfoliation, it is important to note that the quality of the graphene may be lower.⁴¹⁻⁴² The utilisation of LPE techniques is increasingly favoured due to their cost-efficiency, scalability for production, and ability to generate defect-free graphene. Nonetheless, these techniques frequently yield multi-layered graphene.

Chemical Exfoliation or Reduction

Reduced graphene oxide represents another iteration of graphene achieved through chemical exfoliation, as detailed in section 1.5. The chemical reduction process involves subjecting graphite to potent oxidizing agents to disintegrate the layers and produce graphene oxide. Subsequently, the graphene oxide can be reintegrated into graphene through chemical or thermal means. While this approach can yield substantial quantities of graphene, the quality may not meet that of mechanically exfoliated graphene.⁴³

1.3.5.2. Bottom-Up Approaches

Bottom-up methods involve constructing graphene from smaller carbon-containing molecules, essentially assembling it atom by atom or molecule by molecule. This approach generally results in higher yields but may introduce structural defects or variations depending on the specific method used.

Chemical vapor deposition (CVD)

This method involves depositing carbon atoms onto a substrate from a gas phase. The growth conditions can be carefully controlled to produce high-quality graphene films.¹⁴ This is a high-cost method that can require a temperature as high as 1000 °C, with a hydrocarbon gas flow as a precursor.⁴⁴ CVD utilises high temperatures and hydrocarbon gas to grow graphene on transition metals (Fe, Co, Ni, Cu, Pd). This method involves saturating the metal surface with carbon atoms, resulting in well-ordered graphite films with thicknesses ranging from a few graphene layers to 1.5 nm. This is the most promising method for large-scale production of graphene. In CVD, carbon-containing gases are decomposed on a heated substrate, causing graphene layers to grow.³⁷ While not

without drawbacks in terms of cost and complexity, this approach shows potential for the large-scale manufacture of high-quality graphene.

Epitaxial growth

This approach entails the growth of graphene on a single-crystal substrate, such as silicon carbide. It yields high-quality graphene with controlled properties, albeit it involves a complex process. ¹⁴ By annealing SiC at high temperatures under vacuum, silicon sublimates, leaving behind a graphitic surface ideal for graphene growth. This method produces high-quality graphene with excellent electronic properties, making it a potential candidate for high-end electronics with superior speed, feature size, and power consumption compared to silicon. However, achieving high production rates remains a challenge.^{37,45}

The unzipping of carbon nanotubes

This method involves cutting open carbon nanotubes to produce graphene nanoribbons. This can be a good way to produce graphene with specific properties, but the yield is typically low. This highlights a promising approach for tailoring CNTs into versatile graphene nanoribbons.³⁷

Other methods for producing graphene include the electrochemical exfoliation and the arc discharge process.³⁷

1.3.5.3. Synthesis of Graphene and Graphene Aerogel Materials

A collaborator involved in the SITS project has developed an innovative method for synthesizing graphene materials, utilizing a detonation-based process that differentiates it from conventional synthesis techniques. This method commences with the controlled detonation of carbon-containing precursors, such as hydrocarbons. The high-energy nature of this process yields crumpled and porous graphene structures with sub-100-nanometer particle sizes, which are essential for applications in printed electronics.⁴⁶

Subsequent to the synthesis, the graphene is subjected to liquid-phase exfoliation, which facilitates the production of a stable colloidal suspension. This enables the formulation of graphene inks suitable for various applications. For instance, the graphene aerosol gel ink produced through this method has been successfully employed to print interdigitated electrode micro-supercapacitors on flexible polyimide substrates. These printed devices exhibit excellent electrochemical stability and capacitive retention, thereby underscoring the potential of this synthesis method for scalable, high-performance graphene-based printed electronics and energy storage systems.

Integrating detonation synthesis with liquid-phase exfoliation provides an efficient and scalable method for graphene production, making it a promising alternative to current synthesis techniques.

1.3.6. Applications

Graphene is a highly versatile material renowned for its remarkable properties, making it applicable in a wide range of fields including electronics, composite materials, energy storage, sensors, biomedical applications, optoelectronics, water filtration, and flexible electronics.³⁷

Currently, materials research is focused on the production and characterisation of thin carbon films, with the goal of developing successful applications for this promising material. Two decades of research have yielded a number of exciting possibilities, including long-lasting batteries for mobile devices, more efficient solar cells, corrosion prevention coatings, protein-friendly hair dye, water purification devices, display panels, and highly sensitive sensors.²⁰

One of the most promising applications for graphene is in high-speed electronics, where its exceptional conductivity makes it an ideal material. However, electronic devices require semiconductors with small yet significant band gaps, which graphene currently lacks. Despite this, in

recent years scientists have been working on creating graphene derivatives with a band gap for commercial purposes.²⁰

Another area of focus for graphene is electrochemical sensing, particularly electrochemical analysis. While graphene's exclusive

structure presents challenges with electron transfer kinetics, it has already been used to detect single gas molecules and biological agents in the body. Researchers are also exploring the use of graphene-based sensors in the agriculture industry to improve efficiency and productivity.⁴⁷

1.3.6.1. Graphene as an Electrode

In recent years, researchers have developed graphene-based nanosensors. These sensors can measure physical quantities and detect various gases, chemical species, viruses, and bacteria. Graphene's mechanical and electrochemical properties make it a promising material for building nano-electromechanical system devices.⁴⁸

Graphene and related materials offer new possibilities to electrochemical systems. Electrochemistry utilises energy in its cleanest form, electricity, to collect or inject electrons through electrodes. It is at the core of many chemical and biological sensors and energy storage and generation technologies. Doping graphene with heteroatoms is a popular method to enhance its electrochemical performance. Graphene-based materials have been used in various electrochemical sensors, including voltammetric, potentiometric, and electrochemical impedance spectroscopy. The recent literature indicates that the use of graphene in electrochemical applications is rising. In recent years, graphite and graphene materials have been utilised to create screen-printed electrodes for cyclic voltammetry analysis.⁴⁹

1.3.6.2. Energy Storage

Graphene's versatility has enabled researchers to employ it in various ways in batteries, including as anodes and additives, to enhance performance. Graphene exhibits remarkable potential in the field of batteries, resulting in numerous advantages, such as longer lifespan, faster charging, increased flexibility, and reduced weight compared with conventional batteries.⁵⁰

Graphene supercapacitors have the potential to transform energy storage for quick bursts of power. Ongoing research shows promise for the future due to graphene's exceptional conductivity, allowing it to charge and discharge at lightning-fast speeds. They can outperform traditional batteries in delivering an impressive amount of power in a short amount of time.⁵⁰

1.3.6.3. Graphene in Smart Farming Applications

Research has been conducted on graphene-based sensors in precision agriculture. These sensors enable real-time monitoring of soil nutrients, moisture, and pathogens, which promotes the adoption of targeted fertilisation and irrigation techniques. Furthermore, graphene nanomaterials are being studied for their ability to enhance plant growth by stimulating nutrient uptake and boosting pest resistance.⁵¹⁻⁵²

Another exciting area of graphene's potential in agriculture is water purification and wastewater treatment. Ongoing research in this field is focused on exploring the use of graphene filters and purifiers to promote sustainability and resource efficiency by providing clean water for irrigation and treating agricultural wastewater.⁵⁰

Biocompatibility Issues of Graphene in Agriculture

Studying the biocompatibility and potential risks associated with graphene in agriculture is important. One area of concern is toxicity, which can be assessed by studying the impact of different types and dosages of graphene on soil organisms and plant health. Another risk is bioaccumulation, which can lead to long-term harm. Therefore, it is vital to consider the potential for graphene nanomaterials to accumulate in soil or plant tissues. Also, it is important to track the movement and degradation of graphene in agricultural environments to understand its potential impact on ecosystems.⁵³

Another aspect to consider is the degradation and lifecycle assessment of graphene. Factors such as temperature, microbial activity, and sunlight exposure can influence the degradation pathways of graphene in soil and water. Therefore, it is essential to identify these factors to gain a better understanding of the degradation process. Furthermore, assessing the environmental footprint of graphene production and use in agriculture is crucial. This can be done by conducting a lifecycle analysis that takes into account energy consumption, resource depletion, and waste generation.⁵⁴

Obstacles and Limitations for Applications of Graphene in Agriculture

A key obstacle to utilising graphene in agriculture is its scalability and cost-effectiveness. To overcome this challenge, there is a demand for cost-efficient and scalable approaches to graphene synthesis, such as utilising biomass or agricultural waste as precursors.

Another challenge is integrating graphene-based sensors into existing agricultural machinery and irrigation systems. Smaller, low-power sensors that can be seamlessly integrated into current infrastructure are required to tackle this issue. To ensure the successful implementation of graphene in agriculture, standardisation, and regulations are imperative. This includes establishing safety guidelines, engaging with the public, developing regulatory pathways, and implementing sustainable and environmentally friendly production methods for graphene in agriculture.

While the focus of this thesis is on fundamental studies rather than applications, the insight into properties from this study will be useful in developing sensors for agricultural applications in the SitS project.

1.4. GRAPHENE OXIDE

Graphene oxide is a chemically modified form of graphene. It comprises carbon atoms arranged in a graphene-like two-dimensional lattice structure with oxygen-containing functional groups (epoxides, hydroxyls, and carboxyls) on its basal plane and edges.

1.4.1. Overview of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

Compared to mechanically exfoliated graphene, solution-based synthesis of Reduced graphene oxide (rGO) produces smaller and more irregular structures. rGO sheets are generally referred to as chemically reduced from Graphene oxide (GO).⁵⁵ Graphene oxide (GO) is produced by oxidising graphite powder with strong acids and oxidants. This process creates oxygen-containing groups on the material's surface. Reduced graphene oxide (rGO) is then derived from GO by removing some of these oxygen groups through a reduction process. This difference in oxygen content significantly affects the electrical properties of the materials.⁵⁶ The chemical composition of fully oxidised graphite oxide is approximately C4O(OH).⁵⁶ Graphite oxide is highly hydrophilic and can be easily exfoliated by sonication in water, producing stable dispersions consisting mostly of single-layer sheets, known as GO. GO has a C:O ratio of 2.0 to 2.9, a layered structure with a large spacing of 0.6-1.1 nm, it is highly hydrophilic, an insulator and consists mostly of single-layer sheets after exfoliation. On the other hand, rGO has reduced oxygen content compared to GO; it is conductive but with lower conductivity than graphene, and the electron transport occurs via hopping between non-oxidized graphene islands.^{14,57,58}

The atomic structures of GO and rGO are still debated due to a random distribution of functional groups in GO and rGO layers and compositional variations depending on the preparation method used¹⁴ Their representative structures are shown in Figure 1.9. AFM analysis has shown that the layer height of GO is approximately 1.1 ± 0.2 nm.⁵⁷



Figure 1.9. Representative Chemical Structures of (a) Reduced Graphene Oxide and (b) Graphene Oxide, Drawn Using Avogadro Software.¹⁹

1.4.2. Synthesis of GO and rGO

Graphene oxide (GO) can be produced by oxidising graphite and then exfoliating the resulting graphite oxide.⁵⁹ Early methods of graphene oxide synthesis included Brodie's method (BR-GO), which used potassium chlorate and nitric acid to yield soluble GO with a C/O ratio of 2.2.^{57,60} Staudenmaier's method (ST-GO) was a modification of Brodie's method that used sulfuric acid, resulting in faster production but similar properties to BR-GO.⁶¹ Hofmann's method (HO-GO) used potassium chlorate

and non-fuming nitric acid and produced GO with lower oxygen content, resulting in a higher C/O ratio of 2.5.^{59,62}

The most popular method is the Hummers Method (HU-GO), which uses potassium permanganate, sulfuric acid, and sodium nitrate. This method is fast and safe, but it is not eco-friendly due to the emission of NO_x . There are several modified versions of the Hummers method, including nitrate-free, two-step, co-oxidant, and low-temperature methods.^{57,59}

A more modern GO synthesis method is the Tour's method, also known as TO-GO, which was developed in 2010 and uses permanganate and phosphoric acid. This method is considered safer than the Hummers method and produces a higher yield of GO with a regular structure and higher oxidation. However, chemical methods often damage the GO structure due to harsh conditions and impurities, which may make the resulting GO unsuitable for electronic applications due to poor electrical properties.^{57,63}

To overcome these limitations, modern trends focus on modifying existing methods, such as Tour's method, by reducing the reaction time. Additionally, researchers are exploring electrochemical synthesis as an eco-friendly alternative for better GO quality.⁵⁷

1.4.3. Properties

Graphene oxide possesses several interesting properties, such as its ability to disperse easily in water and other polar solvents due to its hydrophilic nature. It also retains a layered structure that is similar to graphene, with interlayer spacing affected by oxygen groups. Additionally, oxygen groups enable easy modification and functionalisation of the material, thus allowing for tunable surface chemistry. Furthermore, graphene oxide can be reduced to produce rGO, which exhibits enhanced electrical conductivity.

Graphene oxide contains a mixture of sp² and sp³ hybridised carbon atoms that are functionalised with oxygen-containing groups. As mentioned, these functional groups include hydroxyl (C–OH) and epoxide (C–O–C) functional groups on the basal plane and carbonyl (C=O) and carboxyl (COOH) groups at the sheet edges, as depicted in Figure 1.9.⁶⁴ These functional groups introduce sp³ defect sites to the nanosheets, distorting the intrinsic conjugated π system and lowering the overall strength and conductivity. The sp³ carbon atoms bonded to oxygen make GO an insulator. Graphene oxide is an electronically hybrid substance that displays both a large energy gap between the σ -states of its sp³ bonded carbons and conducting π -states from sp² carbon sites.³⁷ The properties of graphene oxide (GO) are significantly influenced by the synthesis techniques employed, which dictate the quantity and variety of oxygen-containing groups within the material. Unlike graphene, GO is hydrophilic, enabling it to easily form stable suspensions in water, a key feature that distinguishes it in various applications. GO materials with extensive oxidation are electrical insulators and possess a bandgap of $\geq 2.2 \text{ eV}$.⁵⁷ rGO generally exhibits superior conductivity in comparison to GO owing to the elimination of oxygen-containing groups. Nevertheless, attaining a high degree of reduction while preserving an optimal structure poses a notable challenge.⁵⁷

1.4.4. Applications

Graphene oxide is a versatile material with many potential applications, particularly in materials science, biomedicine, and environmental technology. Ongoing research and development in this area promise to expand its utility further and understand its environmental and health implications.

Recent research indicates that GO is increasingly being utilised in electronic devices and sensors. With its transparency and moderate electrical conductivity, GO is suitable for use in transparent conductive films for applications such as touchscreens, solar cells, and flexible electronics. Additionally, GO's high surface area makes it well-suited for developing sensors capable of detecting gases and biomolecules. GO can also be incorporated into polymer composites to enhance their strength, conductivity, and barrier properties.⁵⁷

The electrical conductivity lost during the formation of GO is partially recovered in rGO, giving it similar potential applications to graphene, such as in electronics, conductive inks, and composite materials. The performance of rGO in these applications is heavily influenced by its quality. Additionally, the high surface area of both GO and rGO makes them well-suited for use in energy storage devices, such as supercapacitors and lithium-ion batteries.^{57,65}

Graphene materials analysed experimentally in this thesis contain oxygen, and therefore can be classified as reduced graphene oxide. Computational studies in this work investigated a wide range of oxygen concentrations, from reduced graphene oxide to graphene oxide, to find out the effect of the oxygen concentration on electronic properties.

1.5. GRAPHENE NANORIBBONS

In order to effectively incorporate graphene into semiconducting nanoelectronics, it is crucial to create graphene nanoribbons (GNRs) with a width of less than 10 nm. This increased confinement leads to the emergence of a significant band gap, typically ranging from 0.5 eV to 3.0 eV, depending on the ribbon's width and edge structure.⁶⁶ The size of the band gap is heavily influenced by the widths of the nanoribbons and their atomic edge structures. For instance, GNRs terminated with armchair edges can be either metallic or semiconducting, depending on the width of the ribbon.¹⁴ Figure 1.10 illustrates the structures of armchair and zigzag GNRs. The width of each ribbon is defined by the number of carbon atoms (N_A or N_Z) along its edge.



Figure 1.10. Structures of Graphene Nanoribbons (GNRs) are Shown: (a) Armchair GNR and (b) Zigzag GNR.

1.5.1. Synthesis

Various techniques have been developed to create graphene nanoribbons by "unzipping" carbon nanotubes (CNTs). These techniques involve processes such as plasma etching of partly embedded CNTs, solution-phase oxidative processes, and catalytic cutting of CNTs. In one method, multiwalled CNTs were partly embedded in a polymer film and then subjected to Ar plasma etching.⁶⁷ This process removed the unprotected side walls of the CNTs, leaving behind single-, bi-, and multi-layer GNRs, depending on the number of walls of the original CNTs and the etching time. The resulting GNRs had smooth edges and widths between 10 and 50 nm, but some disorder was detected at the edges. Aligned GNR arrays can be obtained by using Ar-plasma etching to "unzip" partially embedded and horizontally aligned CNTs. This method can produce narrower GNRs with a width distribution of 2–8 nm.^{14,68}

1.5.2. Properties of nanoribbons

The development of graphene electronics poses a significant challenge, as graphene lacks a band gap and electrons cannot be confined through Klein tunnelling. However, by patterning graphene into thin nanoribbons, it is possible to engineer a band gap. Reducing the lateral dimensions of a graphene material can open a band gap, with the size determined by the state of the edge and the nanoribbon's width. According to tight-binding calculations, GNRs with 'armchair' edges can be metallic or semiconducting, with the size of the band gap inversely proportional to the width of the ribbon, while those
with 'zigzag' edges are always metallic.¹⁴ Tuning the width of armchair nanoribbons can help achieve band gaps similar to commonly used semiconducting materials.

Hypothetically, ordered arrangements of oxygen atoms can cut graphene into nanoribbons. In this thesis, we investigated some examples of graphene nanoribbons generated by specific positions of epoxide groups.

1.6. GRAPHENE WITH DEFECTS

In the realm of graphene's electrical and optical properties, defects - or deviations from the ideal lattice structure - are extremely important. These defects can take various forms, including point defects, line defects, and planar defects. Point defects, for instance, involve individual atoms or small groups within the lattice, with vacancies (absent carbon atoms, Figure 1.11 (a)) acting as electron scattering centres and reducing conductivity, and interstitials (additional atoms wedged within the lattice) potentially enhancing or hindering conductivity depending on their type. Line defects, meanwhile, disrupt the lattice along a line, with grain boundaries (interfaces between regions with different crystal orientations) causing electron scattering and altering mechanical properties and dislocations (missing or extra atomic planes), introducing strain and weakening the material. Lastly, planar defects affect larger areas of the lattice, with wrinkles and ripples (out-of-plane undulations) modifying electronic properties and introducing strain, and folds and tears significantly impacting mechanical strength.⁶⁹⁻⁷⁰⁻⁷¹



Figure 1.11. Point Defects in Graphene: (a) Vacancy, (b) Stone-Wales (5775) defect, (c) Oxygen Substitution

1.6.1. Stone–Wales defects

A Stone-Wales (SW) defect is a type of crystallographic defect that occurs in graphene when two carbon atoms rotate 90 degrees, resulting in a change in connectivity between the atoms (Figure 1.11 (b)), generating pentagons and heptagons from some of the hexagons in graphene.⁷²⁻⁷³⁻⁷⁴ The SW defects behave as preferential adsorption centres for hydrogen and other chemical elements, which is important for several applications ⁷⁵ Stone-Wales defect has a formation energy (Ef) of approximately 5 eV, according to a review from 2011.⁷³

1.6.2. Single vacancy defects

A vacancy in graphene is created when one carbon atom is missing, resulting in a single vacancy (SV), Figure 1.11 (a). This creates three dangling bonds (or undercoordinated atoms) around the vacancy. Two of the three undercoordinated atoms link to each other, while the third atom remains undercoordinated due to geometric constraints. The formation of this defect demands more energy than the Stone-Wales defect since it includes a dangling bond. According to computations, the formation energy, Ef, is approximately 7.5 eV.^{73,76}

1.6.3. Multiple vacancy defects.

Double vacancy (DV) means the coalescence of two single vacancies (SVs) or the removal of two neighbouring carbon atoms. Theoretical calculations estimate the formation energy of a DV defect to be around 8 eV, which is lower than the energy required for two SVs. Interestingly, despite this lower energy cost, experimental observations suggest that DVs might be more prevalent than SVs.⁷³

1.6.4. Oxygen substitution

Oxygen-containing carbon nanomaterials such as graphene oxide and oxidised carbon nanotubes can be used in the next generation of nanoelectronics. However, the structure and properties of O defects in graphene are poorly understood. Both recent and earlier studies have shown different configurations of substitutional oxygen in the hexagonal lattice.^{77,78} Substitutional oxygen acts as an *n*-type dopant in graphene, which creates asymmetric conduction in the material. Holes are scattered more strongly than electrons, making the behaviour of these impurities different from the out-ofplane oxygen-containing functional groups bonded to graphene. This demonstrates how different types of C and O bonds can affect the electronic properties of sp² carbon allotropes, as demonstrated in numerous previous works.⁷⁸⁻⁷⁹

The synthesis procedure used by our collaborators is likely to produce defects. Therefore, as part of the theoretical investigation, we modelled graphene with vacancies and oxygen-filled vacancies (substitutional oxygen).

1.7. GRAPHENE AEROGELS

To fully exploit the properties of graphene, it is crucial to develop methodologies for converting the 2D material into 3D structures. Therefore, preparing and analysing graphene materials with threedimensional (3D) structures, including aerogels, hydrogels, and macro-porous films, is necessary.⁸⁰ Carbon aerogels are a class of porous nanomaterials with various applications. Among them, graphene aerogels (GA) are particularly intriguing materials composed primarily of graphene sheets with exceptional properties that hold significant promise for a wide range of applications.

1.7.1. Structure and Properties

GA are porous nanomaterials composed of aggregates of graphene sheets with a 3D structure that exhibit high surface area, tunable porosity, large pore volumes, and low density. GA boast impressive mechanical strength despite their low density. This is attributed to the strong covalent bonds within the graphene sheets and the reinforcing network of carbon nanotubes.⁸¹ These aerogels are porous, and the size and shape of the precursor nanoparticles determine their porosity. Micropores are related to the intra-particle structure, while meso- and macropores are related to the inter-particle structure.⁸² The exact arrangement of graphene sheets in this 3D network remains an active area of research. The structure is likely disordered, with varying pore sizes and sheet connections.

1.7.2. Synthesis

Hydrothermal reduction

The hydrothermal reduction of GO is commonly used to produce graphene hydrogels. The method involves self-assembly of graphene sheets, and after supercritical drying or freeze drying, a GA is obtained which leads to the formation of 3D graphene structures. High temperature and pressure conditions are required, and the gel rate is controlled to maintain gel integrality.⁸³

Chemical reduction

One of the most conventional and cost-effective methods for restoring the sp² network in GO is chemical reduction. This approach uses mild reduction agents and is generally considered superior to hydrothermal reduction, which relies on high temperatures, high pressures, and chemical cross-linkers. However, the chemical reduction method can result in smaller surface areas due to graphene layers restacking through a π - π interaction. Additionally, the use of toxic chemicals, such as hydrazine, contradicts the goal of preserving the environment and can have negative effects in bio-related applications. Therefore, researchers have been exploring milder and more eco-friendly alternative methods.⁸³

Cross-linking methods such as Hydrogen bonds

GO dissolves well in water but not in strong acidic aqueous media. If the pH of the GO solution is decreased, it forms a stable gel. Cross-linking agents help this process by strengthening the bonding between the GO sheets. Common cross-linkers are hydroxyl and oxygen-containing groups.⁸³

There are various other approaches to producing GA, including polymerisation, where monomers are polymerised in the presence of graphene oxide to form a composite aerogel. Another method is template-directed reduction, where graphene oxide is deposited onto a sacrificial template that is then removed, resulting in the desired aerogel structure. Additionally, modern techniques like direct ink writing and stereolithography enable the creation of intricate 3D structures using graphene aerogel inks.⁸³

Printing of Graphene Aerogels

According to a recent review, two methods for 3D printing GA are used: Direct ink writing (DIW) and Stereolithography (SLA). Both of these techniques involve building the structure layer-by-layer.⁸³ 3D Printing of Graphene Aerogels offers many advantages, such as design freedom, complexity, and high durability.

Direct Ink Writing (DIW)

DIW is a method that involves the extrusion of liquid ink, which solidifies rapidly. To ensure good shape retention, high-viscosity inks are needed. DIW offers the flexibility to use various ink compositions, including multiple materials. Some examples of DIW applications include ultralight graphene aerogel micro-lattices with Ca²⁺ ions for gelation, graphene-ethanol ink with (ethylene glycol butyl ether) EGB dispersant and DBP/PVB thickening agent, and graphene-biopolymer aerogels for water decontamination. EGB dispersant is a material that helps prevent the graphene particles from clumping together in the ink and, DBP/PVB thickening agent is a combination of two chemicals (dibutyl phthalate and polyvinyl butyral) that increase the viscosity of the ink, making it suitable for DIW.^{83,84} This method is unfortunately not very accurate for dimensional control of complex patterns and requires the availability of small nozzles for nano-inks.

Stereolithography (SLA)

SLA uses laser light to cure photopolymer resin layer by layer. This process requires a fast-solidifying resin with low viscosity to create high-resolution models. A complex micro-architected graphene (MAG) aerogel using XGO (crosslinked graphene oxide) resin is an example of what can be made using this technology. SLA has many advantages. It can produce intricate and high-resolution structures with nearly arbitrary shapes. However, compared to DIW, it has a slower printing speed. SLA is a great option for creating highly detailed and complex 3D models, but it may not be the best option if you need to develop models quickly.^{83,85}

1.7.3. Applications and Potential

Graphene aerogels have a wide range of applications, including energy storage, where they can act as electrodes in both supercapacitors and batteries due to their high surface area and conductivity. Supercapacitors are particularly useful for quickly storing and releasing energy, making them ideal for electric vehicles and portable electronics. GAs can be used as electrodes in various electrochemical devices, such as fuel cells and solar cells. Graphene aerogels also have the ability to absorb large amounts of oil, making them an effective tool for cleaning up oil spills. Additionally, their high adsorption capacity for contaminants makes them an ideal choice for water purification and desalination.^{83,86,87,88}

Graphene-based materials analysed experimentally in this thesis are composed of curved graphene sheets and, therefore, can be classified as graphene aerogels. Computational studies in this work looked at a range of curvatures to determine how the curvature of graphene sheets affects their electronic properties and the interplay of curvature with oxygen functionalisation.

1.8. NANOTUBES

Carbon nanotubes are cylindrical structures of rolled graphite sheets that form a seamless tube. There are two main types of carbon nanotubes: single-walled carbon nanotubes (SWCNTs), which are made up of a single graphene sheet rolled into a cylinder, and multi-walled carbon nanotubes (MWCNTs), which consist of multiple concentric graphene cylinders with an interlayer spacing of 3.4 Å and a diameter typically ranging from 10 to 20 nm. Both types of nanotubes can be several hundred microns or even centimetres long.¹⁴ SWCNTs can exhibit semiconducting or metallic behaviour depending on their structure, while MWCNTs are generally metallic conductors. These properties make both types of carbon nanotubes highly promising materials for various applications, including electronics, composites, energy storage, and sensors. Carbon nanotubes were first discovered by lijima in 1991.⁸⁹ Since then, researchers have explored their fascinating properties and potential applications in various fields.

1.8.1. Structure of Carbon Nanotubes:

As mentioned above, carbon nanotubes are cylindrical structures of graphene sheets rolled up into tubes with nanometre-scale diameters. They are composed of carbon atoms covalently bonded in a sp² hybridised configuration. The structure of a specific nanotube is represented by the (n,m) notation, which specifies the direction and axis along which a piece of graphene is rolled up to form the corresponding tube. CNTs can have different chiralities depending on the combination of n and m, resulting in various structural configurations. Two prominent configurations are zigzag and armchair nanotubes, as illustrated in Figure 1.12.

SWCNTs



Figure 1.12. Single-Walled Carbon Nanotubes (a) Zigzag (b) Armchair (c) Chiral.

1.8.1.1. Zigzag Nanotubes

Zigzag nanotubes have a carbon lattice arrangement resembling a zigzag pattern along the tube's diameter and can be described with notations in the form (n,0). Zigzag CNTs have a bang gap that suggests semiconducting behaviour.

1.8.1.2. Armchair Nanotubes

Armchair nanotubes are named for their resemblance to chair armrests when viewed along their diameter. They are described by the (n,n) notation, where both n values are equal. Crucially, armchair nanotubes are inherently metallic due to their specific atomic arrangement. This metallic property, characterised by the absence of a band gap and free-flowing electrons, makes them attractive for applications in electronics, optoelectronics, and even structural materials.

1.8.1.3. Chiral Nanotubes

Chiral nanotubes are described with the notation (n,m) where n and m are of different magnitudes. Chiral CNTs are semiconductors, meaning they can conduct electricity under certain conditions but not freely like metals. This semiconducting behaviour is directly related to their chirality, which affects their electronic band structure. The specific band gap of a chiral CNT depends on its (n,m) values.

1.8.2. Properties

Carbon nanotubes possess exceptional properties such as unparalleled mechanical strength, high electrical and thermal conductivity, and a large surface area. Unlike their bulk counterparts, such as graphite and diamond, CNTs have exceptional electronic properties that depend on their chirality and diameter, making them ideal for a wide range of potential applications. Some of the most notable properties of CNTs include their exceptional strength, with a tensile strength greater than that of steel, and their excellent electrical conductivity, making armchair nanotubes one-dimensional metals. Furthermore, carbon nanotubes demonstrate exceptional thermal conductivity, rendering them incredibly versatile materials with boundless potential.⁹⁰

1.8.3. Applications of CNTs

Carbon nanotubes have a broad spectrum of uses, such as in electronics for transistors, interconnects, and conductive films. They are also utilised in nanocomposites to improve mechanical, electrical, and thermal properties. Additionally, CNTs are employed in various sensors due to their sensitivity to chemical and physical changes. Moreover, they are utilised in energy storage applications such as supercapacitors, batteries, and fuel cells. In biomedicine, CNTs have potential uses in drug delivery, imaging, and tissue engineering. Lastly, CNTs are used in nanoelectromechanical systems.⁹¹

Nanotubes are of interest as examples of curved graphene-based systems, with the curvature determined by the diameter of the nanotube.

1.9. SENSORS

1.9.1. Phosphate Sensors

Soil health is the foundation for healthy ecosystems and sustainable food production. Monitoring its key parameters is crucial for effective agricultural management and environmental protection. As previously mentioned, one crucial aspect of soil health is its nutrient content, in particular phosphate, a mineral vital for plant growth. As critical as soil health is, phosphate pollution in water also poses a significant environmental challenge. Regulations mandate the monitoring of phosphate levels in both wastewater and natural water bodies. The conventional approach to phosphate measurement involves a colourimetric technique, which is labour-intensive and reliant on consumables. However, sensors present a promising alternative for phosphate detection, offering the potential for continuous, real-time monitoring. Synthetic receptors and Molecularly Imprinted Polymers (MIPs) were explored for phosphate detection in water.⁹²

Synthetic receptors refer to molecules designed to imitate natural receptors for phosphate ions. These receptors are engineered to bind specifically to phosphate, with the aim of excluding other ions. One advantage is selectivity, as they can be tailored to preferentially target phosphate ions over other ions in the surrounding environment, thereby enabling more precise detection. Another benefit is the potential for miniaturisation, given their controllable size and structure, allowing for potential integration into compact sensor devices for field applications. However, there are limitations to consider. One challenge is the integration with transducers, as many synthetic receptors have not been combined with devices capable of converting the binding event into a measurable signal, such as an electrical or optical signal, which is essential for practical sensor applications. Additionally, there are selectivity challenges, as while these receptors can be designed for phosphate, similarly sized anions, like sulphate, can still interfere with phosphate detection, consequently reducing accuracy.^{92,93}

MIPs are another sensing method that have been studied. These polymers are synthesised to contain cavities that are imprinted by a target molecule, such as phosphate. Even after the target molecule is removed, these cavities retain their specific shape and binding sites, allowing them to bind to the target molecule multiple times. The advantages of MIPs include high specificity, as the imprinted cavities make them highly specific to phosphate, and potential durability, as they can be more robust than some natural receptors, potentially offering longer sensor lifetimes compared to biological components. However, there are some limitations. For instance, many MIPs, such as synthetic receptors, have not been integrated with transducers for practical use. Additionally, while some MIPs for phosphate detection have been developed, many are still in the research phase, requiring further refinement before widespread use. ^{92,94}

1.9.2. Graphene-Based Sensors

Graphene is gaining rapid traction in sensor development due to its many advantages. This material shows promise for highly sensitive and versatile sensors. Researchers are exploring the use of graphene in a variety of applications, including the quantitative detection of biomolecules, antigens, antibodies, antibiotics, chemicals, narcotics, toxins, DNA, whole-cell viruses, bacteria, environmental monitoring, and gas detection.⁹⁵⁻⁹⁶

Graphene-based electrochemical sensors have garnered significant attention due to their ability to detect changes in current or voltage when specific molecules or ions interact with the electrode surface. These sensors are highly valued for their specificity, sensitivity, stability, affordability, and low detection limits. When a target molecule binds to the sensor surface, the interaction is converted into an electrical signal. Ongoing research focuses on developing new types of graphene electrochemical biosensors with ultra-high sensitivity, as graphene's exceptional conductivity and biocompatibility make it ideal for easy conjugation with biological molecules.⁹⁷ Graphene's incorporation significantly improves the sensitivity of electrochemical sensors.

This enhancement can be observed in various applications, as demonstrated by Suprem et al. in developing an electrochemical sensor for phosphate detection. They utilized a high-quality graphene nano-ink to fabricate printed sensors with a microplotter, overcoming challenges related to detecting phosphate ions. Their sensors showed a sensitivity of $0.3223 \pm 0.025 \ \mu\text{A} \ \mu\text{M}-1 \ \text{cm}-2$ and a low limit of detection of 2.2 μ M. Additionally, they exhibited high selectivity for phosphates, even with interfering ions like NO3–, CO3–, Cl–, and SO42–. This work underscores the potential of graphene-based sensors in environmental monitoring, particularly for phosphate detection.⁹⁸

1.10. RESEARCH AIMS

1.10.1. PhD Project Aim:

This PhD employs ultrafast spectroscopy and computational modelling to explore the properties of graphene and its derivatives. In particular, this research aimed to investigate the properties of graphene materials synthesised by our partners within the SitS project for use in phosphate sensors to understand how the properties of these graphene-based materials are related to their structure and how these fundamental properties may affect these materials' performance in sensors.

1.10.2. Research Techniques

Experimental Techniques

This research employed a range of experimental techniques to investigate the structural and functional properties of graphene-based materials. Spectroscopic methods, including ultraviolet-visible and infrared spectroscopy, provided detailed insights into its structural characteristics, bonding configuration, and absorption behaviour. X-ray photoelectron spectroscopy provided evidence regarding elemental composition and the presence of oxygen functionals present in the graphene-based film samples. Electron microscopy techniques offered a comprehensive understanding of the morphology and surface topography. Finally, transient absorption spectroscopy enabled the study of electron dynamics on ultrafast timescales.

Theoretical Methods

This research employed molecular modelling using Density Functional Theory. Software packages SIESTA and Gaussian were utilised in these simulations to explore graphene derivatives structures and their electronic and optical properties.

Through combining experimental data and theoretical models, this research reveals the significance of graphene materials for novel applications and demonstrates the added value of multidisciplinary exploration.

1.11. REFERENCES

¹ UKRI. (2022). *GtR*. Ukri.org. <u>https://gtr.ukri.org/projects?ref=NE/T010924/1</u>

² United Nations. (2019, June 17). Growing at a slower pace, world population is expected to reach 9.7 billion in 2050 and could peak at nearly 11 billion around 2100 | UN DESA | United Nations Department of Economic and Social Affairs. UN DESA | United Nations Department of Economic and Social Affairs. https://www.un.org/development/desa/en/news/population/world-population-prospects-2019.html

³ Yadav, S., Kaushik, A., Sharma, M., & Sharma, S. (2022). Disruptive Technologies in Smart Farming: An Expanded View with Sentiment Analysis. AgriEngineering, 4(2), 424–460. <u>https://doi.org/10.3390/agriengineering4020029</u>

⁴ Sharma, V., Tripathi, A. K., & Mittal, H. (2022). Technological revolutions in smart farming: Current trends, challenges & future directions. *Computers and Electronics in Agriculture*, 201, 107217. https://doi.org/10.1016/j.compag.2022.107217

⁵ Sishodia, R. P., Ray, R. L., & Singh, S. K. (2020). Applications of Remote Sensing in Precision Agriculture: A Review. *Remote Sensing*, *12*(19), 3136. <u>https://doi.org/10.3390/rs12193136</u>

⁶ Peng, Y., Xiao, Y., Fu, Z., Dong, Y., Zheng, Y., Yan, H., & Li, X. (2019). Precision irrigation perspectives on the sustainable water-saving of field crop production in China: Water demand prediction and irrigation scheme optimization. *Journal of Cleaner Production*, *230*, 365–377. https://doi.org/10.1016/j.jclepro.2019.04.347

⁷ Delgado, J. A., Short, N. M., Roberts, D. P., & Vandenberg, B. (2019). Big Data Analysis for Sustainable Agriculture on a Geospatial Cloud Framework. *Frontiers in Sustainable Food Systems*, *3*. <u>https://doi.org/10.3389/fsufs.2019.00054</u>

⁸Khan, F., Siddique, A. B., Shabala, S., Zhou, M., & Zhao, C. (2023). Phosphorus Plays Key Roles in Regulating Plants' Physiological Responses to Abiotic Stresses. *Plants*, *12*(15), 2861. https://doi.org/10.3390/plants12152861

⁹ Singh, H., Halder, N., Singh, B., Singh, J., Sharma, S., & Yosi Shacham-Diamand. (2023). Smart Farming Revolution: Portable and Real-Time Soil Nitrogen and Phosphorus Monitoring for Sustainable Agriculture. *Sensors*, *23*(13), 5914–5914. <u>https://doi.org/10.3390/s23135914</u>

¹⁰ Liu, R.-T., Tao, L.-Q., Liu, B., Tian, X.-G., Mohammad, M., Yang, Y., & Ren, T.-L. (2016). A Miniaturized On-Chip Colorimeter for Detecting NPK Elements. *Sensors*, *16*(8), 1234. <u>https://doi.org/10.3390/s16081234</u>

¹¹ Ahmed, N., De, D., & Hussain, I. (2018). Internet of Things (IoT) for Smart Precision Agriculture and Farming in Rural Areas. *IEEE Internet of Things Journal*, *5*(6), 4890–4899. <u>https://doi.org/10.1109/jiot.2018.2879579</u>

¹² Agrahari, R. K., Kobayashi, Y., Tanaka, T. S. T., Panda, S. K., & Koyama, H. (2021). Smart fertilizer management: the progress of imaging technologies and possible implementation of plant biomarkers in agriculture. Soil Science and Plant Nutrition, 67(3), 248–258. <u>https://doi.org/10.1080/00380768.2021.1897479</u>

¹³ Sharma, V., Tripathi, A. K., & Mittal, H. (2022). Technological revolutions in smart farming: Current trends, challenges & future directions. *Computers and Electronics in Agriculture*, 201, 107217. https://doi.org/10.1016/j.compag.2022.107217

¹⁴ Warner, J. H., Schaffel, F., Rummeli, M., & Alicja Bachmatiuk. (2012). *Graphene*. Newnes.

¹⁵ Chan. (2009). *Graphene and graphite materials*. Nova Science Publishers, Cop.

¹⁶ Kroto, H. W., Heath, J. R., O'Brien, S. C., Curl, R. F., & Smalley, R. E. (1985). C60: Buckminsterfullerene. *Nature*, *318*(6042), 162–163. <u>https://doi.org/10.1038/318162a0</u>

¹⁷ Kroto, H. W. (1996, December 7). *Symmetry, Space, Stars and C60* [Review of *Symmetry, Space, Stars and C60*]. https://www.nobelprize.org/uploads/2018/06/kroto-lecture.pdf

¹⁸ Novoselov, K. S. (2004). Electric Field Effect in Atomically Thin Carbon Films. *Science*, *306*(5696), 666–669. <u>https://doi.org/10.1126/science.1102896</u>

¹⁹ Hanwell, M. D., Curtis, D. E., Lonie, D. C., Vandermeersch, T., Zurek, E., & Hutchison, G. R. (2012). Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics*, *4*(1). <u>https://doi.org/10.1186/1758-2946-4-17</u>

²⁰ Randviir, E. P., Brownson, D. A. C., & Banks, C. E. (2014). A decade of graphene research: production, applications and outlook. *Materials Today*, *17*(9), 426–432. <u>https://doi.org/10.1016/j.mattod.2014.06.001</u>

²¹ Berger, C., Song, Z., Li, T., Li, X., Ogbazghi, A. Y., Feng, R., Dai, Z., Marchenkov, A. N., Conrad, E. H., First, P. N., & de Heer, W. A. (2004). Ultrathin Epitaxial Graphite: 2D Electron Gas Properties and a Route toward Graphenebased Nanoelectronics. *The Journal of Physical Chemistry B*, *108*(52), 19912–19916. https://doi.org/10.1021/jp040650f

²² Stoller, M. D., Park, S., Zhu, Y., An, J., & Ruoff, R. S. (2008). Graphene-Based Ultracapacitors. *Nano Letters*, *8*(10), 3498–3502. <u>https://doi.org/10.1021/nl802558y</u>

²³ Schwierz, F. (2010). Graphene transistors. *Nature Nanotechnology*, 5(7), 487–496. <u>https://doi.org/10.1038/nnano.2010.89</u>

²⁴ Pan, F., Ni, K., Xu, T., Chen, H., Wang, Y., Gong, K., Liu, C., Li, X., Lin, M.-L., Li, S., Wang, X., Yan, W., Yin, W., Tan, P.-H., Sun, L., Yu, D., Ruoff, R. S., & Zhu, Y. (2023). Long-range ordered porous carbons produced from C60. *Nature*, *614*(7946), 95–101. <u>https://doi.org/10.1038/s41586-022-05532-0</u>

²⁵ Maffucci, A., & Miano, G. (2014). Electrical Properties of Graphene for Interconnect Applications. *Applied Sciences*, *4*(2), 305–317. <u>https://doi.org/10.3390/app4020305</u>

²⁶ Reich, S., Maultzsch, J., Thomsen, C., & Ordejón, P. (2002). Tight-binding description of graphene. *Physical Review B*, *66*(3). <u>https://doi.org/10.1103/physrevb.66.035412</u>

²⁷ A. H. Castro Neto, Guinea, F., N. M. R. Peres, Novoselov, K. S., & Geim, A. K. (2009). The electronic properties of graphene. *Reviews of Modern Physics*, *81*(1), 109–162. <u>https://doi.org/10.1103/revmodphys.81.109</u>

²⁸ Léon Brillouin. (1930). Les électrons libres dans les métaux et le role des réflexions de Bragg. 1(11), 377–400. <u>https://doi.org/10.1051/jphysrad:01930001011037700</u>

²⁹ Semenoff, G. W. (1984). Condensed-Matter Simulation of a Three-Dimensional Anomaly. *Physical Review Letters*, *53*(26), 2449–2452. <u>https://doi.org/10.1103/physrevlett.53.2449</u>

³⁰ Katsnelson, M. I. (2007). Graphene: carbon in two dimensions. *Materials Today*, *10*(1-2), 20–27. <u>https://doi.org/10.1016/s1369-7021(06)71788-6</u>

³¹ Wallace, P. R. (1947). The Band Theory of Graphite. *Physical Review*, 71(9), 622–634. https://doi.org/10.1103/physrev.71.622

³² Geim, A. K., & Novoselov, K. S. (2007). The rise of graphene. *Nature Materials*, 6(3), 183–191. <u>https://doi.org/10.1038/nmat1849</u>

³³ Feliciano Giustino. (2014). *Materials modelling using density functional theory : properties and predictions*. Oxford University Press.

³⁴ Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., & Sánchez-Portal, D. (2002). The SIESTA method for*ab initio*order-Nmaterials simulation. *Journal of Physics: Condensed Matter*, *14*(11), 2745–2779. <u>https://doi.org/10.1088/0953-8984/14/11/302</u>

³⁵ Origin Pro version 2023b

³⁶ Wu, J., Pisula, W., & Müllen, K. (2007). Graphenes as Potential Material for Electronics. *Chemical Reviews*, 107(3), 718–747. <u>https://doi.org/10.1021/cr068010r</u>

³⁷ Moosa, A. A., & Abed, M. S. (2021). Graphene preparation and graphite exfoliation. *Turkish journal of chemistry*, *45*(3), 493–519. <u>https://doi.org/10.3906/kim-2101-19</u>

³⁸ Choi, W., & Lee, J. (2016). *Graphene*. CRC Press.

³⁹ Zhou, C., Chen, S., Lou, J., Wang, J., Yang, Q., Liu, C., Huang, D., & Zhu, T. (2014). Graphene's cousin: the present and future of graphane. Nanoscale Research Letters, 9(1), 26. <u>https://doi.org/10.1186/1556-276x-9-26</u>

⁴⁰ Allen, M. J., Tung, V. C., & Kaner, R. B. (2010). Honeycomb Carbon: A Review of Graphene. *Chemical Reviews*, *110*(1), 132–145. <u>https://doi.org/10.1021/cr900070d</u>

⁴¹ Nascimento, J. P., Serodre, T., Santos, J. C. C., Paulinelli, L. R., Santos, A. P., Aparício, S., Costa, L. T., & Furtado, C. A. (2021). "Molecular insights into the production of few-layer graphene in N-Cyclohexylpyrrolidone + water mixtures." *Carbon*, *171*, 723–738. <u>https://doi.org/10.1016/j.carbon.2020.09.034</u>

⁴² Zhou, M., Tian, T., Li, X., Sun, X., Zhang, J., Cui, P., Tang, J., & Qin, L.-C. (2014). Production of Graphene by Liquid-Phase Exfoliation of Intercalated Graphite. International Journal of Electrochemical Science, 9(2), 810–820. <u>https://doi.org/10.1016/s1452-3981(23)07758-1</u>

⁴³ Stankovich, S., Dikin, D. A., Piner, R. D., Kohlhaas, K. A., Kleinhammes, A., Jia, Y., Wu, Y., Nguyen, S. T., & Ruoff, R. S. (2007). Synthesis of graphene-based nanosheets via chemical reduction of exfoliated graphite oxide. *Carbon*, *45*(7), 1558–1565. https://doi.org/10.1016/j.carbon.2007.02.034

⁴⁴ Li, X., Cai, W., An, J., Kim, S., Nah, J., Yang, D., Piner, R., Velamakanni, A., Jung, I., Tutuc, E., Banerjee, S. K., Colombo, L., & Ruoff, R. S. (2009). Large-Area Synthesis of High-Quality and Uniform Graphene Films on Copper Foils. *Science*, *324*(5932), 1312–1314. <u>https://doi.org/10.1126/science.1171245</u>

⁴⁵ Ruan, M., Hu, Y., Guo, Z., Dong, R., Palmer, J., Hankinson, J., Berger, C., & de Heer, W. A. (2012). Epitaxial graphene on silicon carbide: Introduction to structured graphene. *MRS Bulletin*, *37*(12), 1138–1147. <u>https://doi.org/10.1557/mrs.2012.231</u>

⁴⁶ Anand, Xiang, W., Arjun Nepal, Wright, J. P., Chen, P., Nagaraja, T., Shusil Sigdel, LaCroix, B., Sorensen, C. M.,
& Das, S. R. (2021). Graphene Aerosol Gel Ink for Printing Micro-Supercapacitors. ACS Applied Energy Materials, 4(8), 7632–7641. <u>https://doi.org/10.1021/acsaem.1c00919</u>

⁴⁷ Pumera, M., Ambrosi, A., Bonanni, A., Chng, E. L. K., & Poh, H. L. (2010). Graphene for electrochemical sensing and biosensing. *TrAC Trends in Analytical Chemistry*, *29*(9), 954–965. <u>https://doi.org/10.1016/j.trac.2010.05.011</u>

⁴⁸ Bogue, R. (2014). Graphene sensors: a review of recent developments. *Sensor Review*, *34*(3), 233–238. https://doi.org/10.1108/sr-03-2014-631

⁴⁹ Brownson, D. A. C., Kampouris, D. K., & Banks, C. E. (2012). Graphene electrochemistry: fundamental concepts through to prominent applications. *Chemical Society Reviews*, 41(21), 6944.
<u>https://doi.org/10.1039/c2cs35105f</u>

⁵⁰ The Graphene Council. (n.d.). Www.thegraphenecouncil.org. <u>https://www.thegraphenecouncil.org/</u>

⁵¹ Garland, N. T., McLamore, E. S., Cavallaro, N. D., Mendivelso-Perez, D., Smith, E. A., Jing, D., & Claussen, J. C. (2018). Flexible Laser-Induced Graphene for Nitrogen Sensing in Soil. *ACS Applied Materials & Interfaces*, *10*(45), 39124–39133. https://doi.org/10.1021/acsami.8b10991

⁵² Xu, X., Liu, F., Jiang, L., Zhu, J. Y., Haagenson, D., & Wiesenborn, D. P. (2013). Cellulose Nanocrystals vs. Cellulose Nanofibrils: A Comparative Study on Their Microstructures and Effects as Polymer Reinforcing Agents. *ACS Applied Materials & Interfaces*, *5*(8), 2999–3009. <u>https://doi.org/10.1021/am302624t</u>

⁵³ Fadeel, B., Bussy, C., Merino, S., Vázquez, E., Flahaut, E., Mouchet, F., Evariste, L., Gauthier, L., Koivisto, A. J., Vogel, U., Martín, C., Delogu, L. G., Buerki-Thurnherr, T., Wick, P., Beloin-Saint-Pierre, D., Hischier, R., Pelin, M., Candotto Carniel, F., Tretiach, M., & Cesca, F. (2018). Safety Assessment of Graphene-Based Materials: Focus on Human Health and the Environment. ACS Nano, 12(11), 10582–10620. https://doi.org/10.1021/acsnano.8b04758

⁵⁴ Lin, H., Buerki-Thurnherr, T., Kaur, J., Wick, P., Pelin, M., Tubaro, A., Fabio Candotto Carniel, Tretiach, M., Flahaut, E., Iglesias, D., Vázquez, E., Giada Cellot, Ballerini, L., Castagnola, V., Fabio Benfenati, Armirotti, A., Sallustrau, A., Taran, F., Keck, M., & Bussy, C. (2024). Environmental and Health Impacts of Graphene and Other Two-Dimensional Materials: A Graphene Flagship Perspective. ACS Nano. https://doi.org/10.1021/acsnano.3c09699

⁵⁵ Eda, G., & Chhowalla, M. (2010). Chemically Derived Graphene Oxide: Towards Large-Area Thin-Film Electronics and Optoelectronics. *Advanced Materials*, *22*(22), 2392–2415. https://doi.org/10.1002/adma.200903689

⁵⁶ Park, S., & Ruoff, R. S. (2009). Chemical methods for the production of graphenes. *Nature Nanotechnology*, *4*(4), 217–224. <u>https://doi.org/10.1038/nnano.2009.58</u>

⁵⁷ Gómez-Navarro, C., Weitz, R. T., Bittner, A. M., Scolari, M., Mews, A., Burghard, M., & Kern, K. (2007). Electronic Transport Properties of Individual Chemically Reduced Graphene Oxide Sheets. *Nano Letters*, 7(11), 3499–3503. https://doi.org/10.1021/nl072090c

⁵⁸ Hummers, W. S., & Offeman, R. E. (1958). Preparation of Graphitic Oxide. *Journal of the American Chemical Society*, *80*(6), 1339–1339. <u>https://doi.org/10.1021/ja01539a017</u>

⁵⁹ Jiříčková, A., Jankovský, O., Sofer, Z., & Sedmidubský, D. (2022). Synthesis and Applications of Graphene Oxide. *Materials*, *15*(3), 920. <u>https://doi.org/10.3390/ma15030920</u>

⁶⁰ Brodie, B. J. A. C. P. (1855). Note sur un nouveau procédé pour la purification et la désagrégation du graphite. *Ann. Chim. Phys*, *45*, 351-353.

⁶¹ Staudenmaier, L. (1898). Verfahren zur Darstellung der Graphitsäure. *Berichte Der Deutschen Chemischen Gesellschaft*, 31(2), 1481–1487. <u>https://doi.org/10.1002/cber.18980310237</u>

⁶² Jankovský, O., Nováček, M., Luxa, J., Sedmidubský, D., Boháčová, M., Pumera, M., & Sofer, Z. (2017). Concentration of Nitric Acid Strongly Influences Chemical Composition of Graphite Oxide. *Chemistry - a European Journal*, 23(26), 6432–6440. <u>https://doi.org/10.1002/chem.201700809</u>

 ⁶³ Marcano, D. C., Kosynkin, D. V., Berlin, J. M., Sinitskii, A., Sun, Z., Slesarev, A., Alemany, L. B., Lu, W., & Tour, J.
M. (2010). Improved Synthesis of Graphene Oxide. ACS Nano, 4(8), 4806–4814. https://doi.org/10.1021/nn1006368

⁶⁴ Lerf, A., He, H., Forster, M., & Klinowski, J. (1998). Structure of Graphite Oxide Revisited||. *The Journal of Physical Chemistry B*, 102(23), 4477–4482. <u>https://doi.org/10.1021/jp9731821</u>

⁶⁵ Mombeshora, E. T., & Edigar Muchuweni. (2023). Dynamics of reduced graphene oxide: synthesis and structural models. *RSC Advances*, *13*(26), 17633–17655. <u>https://doi.org/10.1039/d3ra02098c</u>

⁶⁶ Barone, V., Hod, O., & Scuseria, G. E. (2006). Electronic Structure and Stability of Semiconducting Graphene Nanoribbons. *Nano Letters*, *6*(12), 2748–2754. <u>https://doi.org/10.1021/nl0617033</u>

⁶⁷ Kosynkin, D. V., Higginbotham, A. L., Sinitskii, A., Lomeda, J. R., Dimiev, A., Price, B. K., & Tour, J. M. (2009). Longitudinal unzipping of carbon nanotubes to form graphene nanoribbons. *Nature*, *458*(7240), 872–876. https://doi.org/10.1038/nature07872

⁶⁸ Jiao, L., Wang, X., Diankov, G., Wang, H., & Dai, H. (2010). Facile synthesis of high-quality graphene nanoribbons. *Nature Nanotechnology*, *5*(5), 321–325. <u>https://doi.org/10.1038/nnano.2010.54</u>

⁶⁹ Meyer, J. C., Kisielowski, C., Erni, R., Rossell, M. D., Crommie, M. F., & Zettl, A. (2008). Direct Imaging of Lattice Atoms and Topological Defects in Graphene Membranes. *Nano Letters*, *8*(11), 3582–3586. <u>https://doi.org/10.1021/nl801386m</u>

⁷⁰ Terrones, M., Botello-Méndez, A. R., Campos-Delgado, J., López-Urías, F., Vega-Cantú, Y. I., Rodríguez-Macías, F. J., Elías, A. L., Muñoz-Sandoval, E., Cano-Márquez, A. G., & Charlier, J.-C. (2010). Graphene and graphite nanoribbons: Morphology, properties, synthesis, defects and applications. *Nano Today*, *5*(4), 351–372. https://doi.org/10.1016/j.nantod.2010.06.010

⁷¹ Yazyev, O. V., & Louie, S. G. (2010). Topological defects in graphene: Dislocations and grain boundaries. *Physical Review B*, *81*(19). <u>https://doi.org/10.1103/physrevb.81.195420</u>

⁷² Banhart, F., Kotakoski, J., & Krasheninnikov, A. V. (2010). Structural Defects in Graphene. *ACS Nano*, *5*(1), 26–41. <u>https://doi.org/10.1021/nn102598m</u>

⁷³ Datt Bhatt, M., Kim, H., & Kim, G. (2022). Various defects in graphene: a review. *RSC Advances*, *12*(33), 21520–21547. <u>https://doi.org/10.1039/D2RA01436J</u>

⁷⁴ Ma, J., Alfè, D., Michaelides, A., & Wang, E. (2009). Stone-Wales defects in graphene and other planarsp2bonded materials. *Physical Review B*, *80*(3). <u>https://doi.org/10.1103/physrevb.80.033407</u>

⁷⁵ Chen, L., Hu, H., Ouyang, Yu., Pan, H. Z., Sun, Y. Y., & Liu, F. (2011). Atomic chemisorption on graphene with Stone–Thrower–Wales defects. *Carbon*, *49*(10), 3356–3361. <u>https://doi.org/10.1016/j.carbon.2011.04.043</u>

⁷⁶ A.V. Krasheninnikov, Nordlund, K., Lehtinen, P. O., Foster, A. S., A. Ayuela, & Nieminen, R. M. (2004). Adsorption and migration of carbon adatoms on zigzag carbon nanotubes. *Carbon*, *42*(5-6), 1021–1025. https://doi.org/10.1016/j.carbon.2003.12.025

⁷⁷ Mombeshora, E. T., & Muchuweni, E. (2023). Dynamics of reduced graphene oxide: synthesis and structural models. RSC advances, 13(26), 17633–17655. <u>https://doi.org/10.1039/d3ra02098c</u>

⁷⁸ Aliyev, E., Filiz, V., Khan, M. M., Lee, Y. J., Abetz, C., & Abetz, V. (2019). Structural Characterization of Graphene Oxide: Surface Functional Groups and Fractionated Oxidative Debris. *Nanomaterials*, *9*(8), 1180. https://doi.org/10.3390/nano9081180

⁷⁹ David, Galbiati, M., de, D., Sahalianov, I. Y., Radchenko, T. M., Sun, J., Peña, D., Lene Gammelgaard, Jessen, B. S., Thomsen, J. D., Bøggild, P., Aran Garcia-Lekue, Camilli, L., & Caridad, J. M. (2021). Unraveling the electronic properties of graphene with substitutional oxygen. *2D Materials*, *8*(4), 045035–045035. https://doi.org/10.1088/2053-1583/ac28ab

⁸⁰ Cong, H.-P., Ren, X.-C., Wang, P., & Yu, S.-H. (2012). Macroscopic Multifunctional Graphene-Based Hydrogels and Aerogels by a Metal Ion Induced Self-Assembly Process. *ACS Nano*, *6*(3), 2693–2703. https://doi.org/10.1021/nn300082k

⁸¹ Gorgolis, G., & Galiotis, C. (2017). Graphene aerogels: a review. *2D Materials*, *4*(3), 032001. <u>https://doi.org/10.1088/2053-1583/aa7883</u> ⁸² Yoshizawa, N., Hatori, H., Yasushi Soneda, Hanzawa, Y., Kaneko, K., & Dresselhaus, M. S. (2003). Structure and electrochemical properties of carbon aerogels polymerized in the presence of Cu2+. *Journal of Non-Crystalline Solids*, *330*(1-3), 99–105. <u>https://doi.org/10.1016/j.jnoncrysol.2003.08.041</u>

⁸³ Nassar, G., Daou, E., Najjar, R., Bassil, M., & Habchi, R. (2021). A review on the current research on graphenebased aerogels and their applications. *Carbon Trends*, *4*, 100065. <u>https://doi.org/10.1016/j.cartre.2021.100065</u>

⁸⁴ Lewis, J. A. (2006). Direct Ink Writing of 3D Functional Materials. *Advanced Functional Materials*, 16(17), 2193–2204. https://doi.org/10.1002/adfm.200600434

⁸⁵ Melchels, F. P. W., Feijen, J., & Grijpma, D. W. (2010). A review on stereolithography and its applications in biomedical engineering. *Biomaterials*, *31*(24), 6121–6130. <u>https://doi.org/10.1016/j.biomaterials.2010.04.050</u>

⁸⁶ Wang, C., Fu, Q., & Wen, D. (2018). Functionalization of Graphene Aerogels and their Applications in Energy Storage and Conversion. *Zeitschrift Für Physikalische Chemie*, *232*(9-11), 1647–1674. https://doi.org/10.1515/zpch-2018-1170

⁸⁷ Hong, J.-Y., Sohn, E.-H., Park, S., & Park, H. S. (2015). Highly-efficient and recyclable oil absorbing performance of functionalized graphene aerogel. *Chemical Engineering Journal*, *269*, 229–235. <u>https://doi.org/10.1016/j.cej.2015.01.066</u>

⁸⁸ Ye, S., Liu, Y., & Feng, J. (2017). Low-Density, Mechanical Compressible, Water-Induced Self-Recoverable Graphene Aerogels for Water Treatment. *ACS Applied Materials & Interfaces*, *9*(27), 22456–22464. <u>https://doi.org/10.1021/acsami.7b04536</u>

⁸⁹ Yamaguchi, T., Bandow, S., & lijima, S. (2004). Synthesis of carbon nanohorn particles by simple pulsed arc discharge ignited between pre-heated carbon rods. *Chemical Physics Letters*, *389*(1-3), 181–185. <u>https://doi.org/10.1016/j.cplett.2004.03.068</u>

⁹⁰ De Volder, M. F. L., Tawfick, S. H., Baughman, R. H., & Hart, A. J. (2013). Carbon Nanotubes: Present and Future Commercial Applications. *Science*, *339*(6119), 535–539. <u>https://doi.org/10.1126/science.1222453</u>

⁹¹ Ferrier, D. C., & Honeychurch, K. C. (2021). Carbon Nanotube (CNT)-Based Biosensors. *Biosensors*, *11*(12), 486. <u>https://doi.org/10.3390/bios11120486</u>

⁹² Warwick, C., Guerreiro, A., & Soares, A. (2013). Sensing and analysis of soluble phosphates in environmental samples: A review. *Biosensors and Bioelectronics*, 41, 1–11. <u>https://doi.org/10.1016/j.bios.2012.07.012</u>

⁹³ Bart), & Smith, D. K. (2007). Synthetically accessible, high-affinity phosphate anion receptors. *Chemical Communications*, *29*, 3039–3039. <u>https://doi.org/10.1039/b706227c</u>

⁹⁴ Akimitsu Kugimiya, & Takei, H. (2006). Preparation of molecularly imprinted polymers with thiourea group for phosphate. *Analytica Chimica Acta*, *564*(2), 179–183. <u>https://doi.org/10.1016/j.aca.2006.01.099</u>

⁹⁵ Wang, T., Huang, D., Yang, Z., Xu, S., He, G., Li, X., Hu, N., Yin, G., He, D., & Zhang, L. (2015). A Review on Graphene-Based Gas/Vapor Sensors with Unique Properties and Potential Applications. *Nano-Micro Letters*, 8(2), 95–119. <u>https://doi.org/10.1007/s40820-015-0073-1</u>

⁹⁶ Shahdeo, D., Roberts, A., Abbineni, N., & Gandhi, S. (2020). Graphene based sensors. *Comprehensive Analytical Chemistry*. <u>https://doi.org/10.1016/bs.coac.2020.08.007</u>

⁹⁷ Atta, N. F., Galal, A., & El-Ads, E. H. (2015). Graphene — A Platform for Sensor and Biosensor Applications. *Biosensors - Micro and Nanoscale Applications*. <u>https://doi.org/10.5772/60676</u>

⁹⁸ Nagaraja, T., Krishnamoorthy, R., Asif, M., Lacroix, B., & Das, S. R. (2023). Microplotter-Printed Graphene-Based Electrochemical Sensor for Detecting Phosphates. *ACS Applied Nano Materials*, *6*(21), 20288–20297. https://doi.org/10.1021/acsanm.3c04228 2. Photochemistry, Spectroscopy and Experimental Techniques

CONTENTS

List of Figures			
Abbreviations			
2.1. Photo	ochemistry	49	
2.1.1.	History	49	
2.1.2.	Planck's constant	50	
2.1.3.	The Photoelectric Effect	50	
2.1.4.	Photochemical laws	51	
2.1.4.1.	The Principle of Photochemical Activation, Grotthus-Draper law	51	
2.1.4.2.	Stark-Einstein law	51	
2.1.5.	Electromagnetic radiation	51	
2.1.5.1.	Visible light	52	
2.1.5.2.	Ultraviolet light	52	
2.1.5.3.	X-rays	52	
2.1.6.	Beer-Lambert's Law	53	
2.1.7.	Absorption and Emission	53	
2.1.7.1.	Absorption and Emission Spectrometers	53	
2.1.8.	Photophysical Processes	54	
2.1.8.1.	Decay of Excited States	55	
2.1.8.2.	Fluorescence	55	
2.1.8.3.	Phosphorescence	55	
2.1.9.	Stimulated and spontaneous processes	56	
2.1.9.1.	Spontaneous Absorption	56	
2.1.9.2.	Stimulated emission	56	
2.1.9.3.	Spontaneous emission	56	
2.1.10. L	asers: Light Amplification by Stimulated Emission of Radiation	57	
2.1.12. P	Pi (π) and sigma (σ) orbitals	58	
2.1.13. P	hotoinduced Processes in Semimetals, Metals and Semiconductors	59	
2.1.13.1	. Metals	59	
2.1.13.2	. Semimetals	59	
2.1.13.3	. Semiconductors	60	
2.1.13.4. Processes in Solids60			
Phonons			
Electron-phonon scattering60			
Electron-electron scattering61			
Charg	e Transfer	61	

2.2.	Spectroscopy	62
2.2.2	1. Atomic Spectroscopy	62
2.2.2	2. Molecular Spectroscopy	62
2.3. Sp	ectroscopy Techniques	63
2.3.3	1. Ultraviolet-Visible Spectroscopy	63
2.3.2	2. Fourier Transform Infrared and Attenuated Total Reflectance	64
2.3.4	4. Transient Absorption	64
2.	.3.4.1. Analysis of Pump-Probe Data	66
2.	.3.4.2. ΔA Spectrum	66
	Ground-State Bleach (GSB)	67
	Stimulated Emission (SE)	67
	Excited-State Absorption	67
Tr	ransient Absorption Instrumental Set-Up	68
2.3.	5. X-ray Photoelectron Spectroscopy	68
2.3.6	6. Raman Spectroscopy	69
2.4. Ot	ther CharacteriSation Techniques	70
2.4.3	1 Electron Microscopy	70
2.4.2	2. Scanning Electron Microscopy	70
2.4.3	3. Transmission Electron Microscopy	71
2.4.4	4. Atomic Force Microscopy	72
2.4.	5. Scanning Near-Field Optical Microscopy	72
2.4.6	6. Profilometry: Optical Surface Analysis	72
2.5. Re	eferences	73

LIST OF FIGURES

Figure 2.1. Diagram of the Electric and Magnetic Fields in the Electromagnetic Radiation.

Figure 2.2. Simplified Schematic of (a) Absorption and (b) Emission Spectrometers

Figure 2.3. Simplified Jablonski Diagram of Photophysical Processes.

Figure 2.4. Schematic of the Transitions Occurring in (a) Class III and (b) Class IV Lasers

Figure 2.5. Generic Energy Level Diagram of a Molecule

Figure 2.6. Schematic Diagram of a UV-Vis Spectrophotometer

Figure 2.7. Schematic of the Various Photoinduced Processes in a Solid and their Contribution to the Transient Signal: electron and hole absorption (EA, HA), ground state bleach (GSB), and stimulated emission (SE).

Figure 2.8. (a) Simplified Energy Level Scheme Depicting the Various Electronic Transitions of a Molecular System, (b) Transient Absorption Difference Spectrum Decomposed into GSB, ESA and SE contributions.

Figure 2.9. A simplified Schematic of a Pump-Probe Experiment

Figure 2.10. Schematic of SEM

Figure 2.11. Schematic of TEM

ABBREVIATIONS

AFM	Atomic Force Microscopy
ATR	Attenuated Total Reflectance
CW	Continuous Wave
FFT	Fast Fourier Transform
GSB	Ground-State Bleach
номо	Highest occupied molecular orbital
KE	Kinetic Energy
LEDs	Light-emitting Diodes
LUMO	Lowest unoccupied molecular orbital
NIR	Near Infrared
ΟΡΑ	Optical Parametric Amplifier
SE	Stimulated Emission
SEM	Scanning Electron Microscopy
ТА	Transient Absorption
TAS	Transient Absorption Spectroscopy
TEM	Transmission Electron Microscopy
UV	Ultraviolet
VIS	Visible
XPS	X-ray Photoelectron Spectroscopy

Photochemistry, Spectroscopy and Experimental Techniques

2.1. PHOTOCHEMISTRY

Light is a form of energy that travels in waves. Different wavelengths of light have different energies. Photochemistry is the study of light-matter interaction. It has various applications, from understanding photosynthesis to developing new materials and technologies. Electromagnetic radiation is characterised by its wavelength, frequency, intensity, and direction.¹ Many spectroscopy techniques have been developed to study the effects of electromagnetic radiation on matter, further discussed in section 2.2.

Light absorption is the transfer of energy from light to matter, resulting in a reduction or weakening of the incident beam's intensity when passed through the matter. This absorbed energy excites electrons in the material, causing them to jump to higher energy levels. The pattern of wavelengths absorbed by the material creates a distinctive fingerprint called an absorption spectrum. Both absorption and emission spectra provide complementary information about the energy level separations within the molecule. The extent of absorption depends on the specific atomic structure of the matter. Light absorption can lead to re-emission of light, referred to as fluorescence or phosphorescence, depending on the spin of the excited state, each characterised by different emission lifetimes and yields. If light absorption produces chemically reactive substances, the process is called photo-activation, and a photochemical reaction occurs.

Though light is known for travelling in straight lines through a vacuum, its interaction with matter results in complex behaviours. Reflection, for instance, refers to where light bounces back upon encountering a surface. This principle is harnessed in the creation of mirrors, where the entire light wavefront is reflected. Light can also refract or bend as it travels from one medium to another with differing densities. Additionally, light can be influenced by its passage through narrow openings or around edges, resulting in a phenomenon known as diffraction. This causes the light to spread out and bend slightly. Certain materials possess the remarkable property of double refraction, where a single incoming light beam is split into two separate beams with distinct polarisations. Another critical interaction involves scattering, where light interacts with particles or uneven surfaces, causing its direction to change. Scattered light can maintain its original frequency, a phenomenon known as Rayleigh scattering. Alternatively, it can gain or lose energy, resulting in a shift in its frequency, known as the Raman effect. Light's interaction with matter extends beyond changes in direction. When certain materials are excited by external energy, such as electricity, they can emit light themselves. This principle forms the foundation for light-emitting diodes (LEDs), which convert electrical energy into visible light. Additionally, some materials have the ability to rotate the plane of polarised light, a property measured by a polarimeter. This interaction provides valuable insights into the structure and composition of materials.²

2.1.1. History

Prior to Maxwell, light was understood as a wave phenomenon, but its exact nature remained unclear. In 1865, Maxwell proposed that light is electromagnetic radiation.³ Building on Maxwell's theory, Hertz's experiments in 1887 provided strong evidence for light as electromagnetic radiation by generating and detecting radio waves. He also observed the photoelectric effect during these experiments, which would later be explained by Einstein using the concept of light quanta.⁴ The understanding of the hydrogen atom's emission spectrum saw significant progress. In 1885, Balmer devised a formula to predict the wavelength of lines in atomic hydrogen in the visible range.⁵ Three years later, Rydberg generalised this formula to determine the wavelengths of any lines in the hydrogen emission spectrum.⁶ Lyman's discovery, in 1906, of ultraviolet spectral lines in hydrogen further refined the observed spectrum, prompting a theoretical explanation.⁷ In 1913, Bohr addressed this need by proposing the quantisation of angular momentum in the hydrogen atom's orbiting electron. This groundbreaking concept, a foundation of the Bohr model, paved the way for the development of quantum mechanics by Heisenberg and Schrödinger, which is discussed further in Chapter 3.

2.1.2. Planck's constant

Planck proposed that oscillating dipoles emit or absorb electromagnetic radiation. He introduced the concept of a quantum, hv, representing discrete energy differences ΔE between two levels. Quanta can only be whole number multiples of hv. To calculate the value of h, Planck used the experimental value of cavity spectra (black-body radiation) in the radiant energy-frequency equation. Equation (2.1) is fundamental to spectroscopy and has laid the groundwork for future developments in the field.

$$\Delta E = hv \tag{2.1}$$

The Planck constant, h, is a cornerstone of quantum mechanics, which governs the behaviour of matter and energy at the atomic and subatomic levels. It relates energy and frequency, revealing the amount of energy a photon carries based on its frequency. Here, Planck's constant (h) acts as the crucial link, connecting the classically defined momentum of a particle to its wavelength, a characteristic property of waves. This relationship is expressed in Equation (2.2). ⁸⁻⁹

$$\lambda = h/p \tag{2.2}$$

$$\Delta E = hv = \frac{hc}{\lambda} = hc\bar{v} \tag{2.3}$$

Where $h = 6.626176 \ x \ 10^{-34} \ (Js)$, $c = 2.998 \ x \ 10^8 \ (s)$, $\lambda =$ wavelength (*m*) and \bar{v} is the reciprocal of λ .

2.1.3. The Photoelectric Effect

Electrons can be ejected from a material upon absorption of electromagnetic radiation. In the 19th century, experiments showed that light shining on certain metals causes electrons to be ejected from those surfaces, known as the photoelectric effect. Classical physics predicted that increasing light intensity would increase the rate of electron emission regardless of the light's frequency. However, eventually, some experiments revealed several fundamental differences from classical predictions. The photoelectric effect experiments showed that each material has a minimum frequency, below which no photoelectrons are emitted, regardless of light intensity. The maximum kinetic energy (K_{max}) of photoelectrons depends only on the incident light's frequency, and increasing light intensity only affects the number of emitted photoelectrons, not their individual energies. Eventually, Einstein proposed that light energy exists as discrete packets called photons (the quantisation of light energy). These photons have individual energies, as stated in Equation (2.1). Einstein added to Planck's theory that light, in addition to behaving like a wave, also exhibits particle-like behaviour.^{8,10}

According to Einstein's model of the photoelectric effect, the interaction between light and matter occurs in a quantised fashion. Electromagnetic energy is transmitted in small packets known as photons, which transfer their entire energy to a single electron in a single interaction. This type of discontinuous absorption process means that the electron can either fully absorb the photon's energy and become ejected from the metal, resulting in photoelectric emission, or not absorb any energy at all. The ejected electrons possess kinetic energy (KE).

$$hv = \frac{1}{2}mv^2 + V$$
 (2.4)

Where V = minimum energy needed for the electron to escape a metal surface and $\frac{1}{2}mv^2 = KE =$ kinetic energy the electron possesses after it escapes the surface.

However, not all of the photon's energy contributes to propelling the electron. A portion of the energy is utilised to overcome the binding forces holding the electron within the metal atom. This characteristic energy, denoted by the symbol ϕ , and the *V* in equation (2.4). is known as the work function of the metal. The work function represents the minimum energy required to remove an electron from the metal and varies depending on the specific element with values on average ranging from a few electron volts eV. The remaining energy after overcoming the work function appears as the kinetic energy of the ejected photoelectron, which determines its speed upon leaving the metal surface. Equations (2.4), (2.5) and (2.6), all convey the same energy conservation principle in different ways. Equation (2.4) as mentioned, is the most general form, illustrating the total energy balance. Equation (2.5) specifically addresses the kinetic energy of the ejected electron, while Equation (2.6) emphasises the relationship between the kinetic energy and the work function.⁸

$$K_{max} = hv - \phi \tag{2.5}$$

$$K_{max} + \phi = hv \tag{2.6}$$

where hv is the energy of a photon of the incident light.

2.1.4. Photochemical laws

Comprehending the principles governing the interaction between light and matter plays a pivotal role in spectroscopy. The Grotthus-Draper and Stark-Einstein laws offer crucial insight into the mechanisms of light absorption by molecules and the consequent chemical transformations, processes central to spectroscopic studies. These laws establish the fundamental concepts elucidating the effectiveness and selectivity of photochemical reactions upon exposure to light.

2.1.4.1. The Principle of Photochemical Activation, Grotthus-Draper law

The Grotthus-Draper law suggests that only the light absorbed by a molecule can cause a photochemical change in that molecule. However, this law has a limitation as it has been found that only a specific wavelength of light is responsible for the photochemical change, which is known as the effective light of the photochemical change.¹¹

2.1.4.2. Stark-Einstein law

According to this law, in the primary process, each molecule involved in a reaction is activated by one unit of effective light. This means that there is a direct one-to-one relationship between the number of reacting molecules and the number of quanta of light absorbed. However, it only applies to the primary process. This law suggests that if a species absorbs radiation, then one particle is excited for each quantum of radiation absorbed.¹¹

2.1.5. Electromagnetic radiation

Electromagnetic waves contain two components: electric and magnetic fields that oscillate perpendicular to each other and to the direction of propagation (Figure 2.1). The energy of these waves varies with their frequency and wavelength, which are exclusive to each wave. Despite their varying energies, they all obey the same fundamental principles. These waves are valuable tools to explore everything from the smallest molecules to the largest celestial bodies. Electromagnetic waves are a form of energy that travel at the speed of light in a vacuum and have no mass.



Electromagnetic Radiation

Figure 2.1. Diagram of the Electric and Magnetic Fields in the Electromagnetic Radiation.

Light interacts with molecules through a process called electronic excitation. When the energy of the absorbed light matches the energy gap between two electronic states in a molecule, an electron is promoted to a higher energy level.

2.1.5.1. Visible light

Human vision is confined to the visible portion of the electromagnetic spectrum, ranging from 400 to 700 nm. This sensitivity arises from electronic transitions within atoms and molecules, where absorbed energy excites electrons to higher energy levels. The subsequent relaxation emits photons with specific wavelengths, perceived as colours. Our peak sensitivity lies around 550 nm, corresponding to green light.⁸

2.1.5.2. Ultraviolet light

Ultraviolet (UV) radiation occupies a higher energy region of the electromagnetic spectrum compared to visible light. Its wavelengths range from 100 to 400 nm, rendering it invisible to the human eye. However, solar UV radiation, particularly the UVB band (280-315 nm), exhibits significant biological effects. Exposure to UVB radiation is a known contributor to skin damage and cataracts. The energy difference between electronic states within molecules dictates whether light falls into the UV or visible range.

Crucially, UV radiation possesses higher energy per photon compared to visible light. This property enables UV radiation to induce electronic transitions in molecules that require a larger energy input.⁸

2.1.5.3. X-rays

X-rays occupy a particular region of the electromagnetic spectrum with wavelengths ranging from 0.01 nm to 10 nm. The mechanism behind X-ray production and spectra involves electron deceleration or complete stoppage, which converts the electrons' kinetic energy to X-ray photons. This results in a continuous spectrum that represents electron deceleration with intensity decreasing with energy, as well as discrete peaks that represent electron transitions within target atoms' inner orbitals. These peaks are designated $Ka/K\beta$ and $La/L\beta$ based on specific transitions in different shells.⁸

Moseley's Law plays an important role in understanding X-rays. Moseley's Law states that the *Ka* X-ray frequency is proportional to the square of the atomic number of the element emitting the X-ray. X-rays are used in crystallography, since X-ray wavelength is comparable to interatomic distances. Bragg's equation relates X-ray diffraction to interatomic spacing and angle, enabling determination of crystal structures by analysing diffracted X-ray patterns.⁸

2.1.6. Beer-Lambert's Law

While the Stark-Einstein and Grotthus-Draper laws are photochemical laws, the Beer-Lambert law is photophysical. The Beer-Lambert law describes the relationship between the intensity of light transmitted through a sample, the concentration of the absorbing species within the sample, and the path length of the light through the sample. The Beer-Lambert law describes the relationship between absorbance and the nature of the absorbing matter, quantified by its extinction coefficient, written as equations (2.7) and (2.8). ¹¹⁻¹²

$$A = \varepsilon lc \tag{2.7}$$

Where A= absorbance, ε = molar absorptivity (the distance light travels through samples), c= sample concentration

Absorbance is measured by comparing the intensity of the beam of light as it enters the sample and the intensity as it leaves the sample. I_0 = intensity of light before it is absorbed by the sample and I= intensity of light after absorption.

$$I_0 \to I$$
 (2.8)

The exponential relation between the variables in Formula (2.8) can easily be measured:

$$A = -\log \frac{I}{I_0} \text{ or } \mp \log \frac{I_0}{I} = \varepsilon lc \text{ or } I = I_0 e^{-\varepsilon lc}$$
(2.9)

2.1.7. Absorption and Emission

Absorption, caused by electronic transitions, is a phenomenon in which atoms or molecules absorb electromagnetic radiation when photons match the energy difference between their ground and excited electronic states. The absorption wavelength and energy levels have a relationship that is governed by the Planck formula $\Delta E = hv$. Both molecular vibrations and rotations also affect the absorption spectra, leading to vibrational and rotational energy quantisation and corresponding fine structures in the spectra. Absorption of different types of radiation (UV, visible, infrared) can lead to various processes like electronic transitions, dissociation, and vibrational excitation.¹²

Emission, also caused by electronic transitions, refers to the different relaxation pathways from excited states, including fluorescence (prompt emission) and phosphorescence (delayed emission). This explains the difference in mechanisms and lifetimes due to spin multiplicity changes. The term photoluminescence refers to light emission following absorption, which includes fluorescence, phosphorescence, and chemiluminescence.¹²

2.1.7.1. Absorption and Emission Spectrometers

Absorption and emission spectrophotometers typically consist of a light source, a monochromator, a sample cell, a detector, and a display device. The key difference between absorption and emission spectrophotometers is that in the former, all components - source, monochromator, sample cell, and detector - are in line with the beam of light, while in the latter, a second monochromator and an emission detector align with a slit opening in the sample compartment perpendicular to the light beam. As a result, in an emission spectrophotometer, the sample acts as a secondary source of radiation, and the only light the detector receives is emitted by the sample itself. The schematics and simplified versions of both spectrometers (single beam) are shown in Figure 2.2.



Figure 2.2. Simplified Schematic of (a) Absorption and (b) Emission Spectrometers.

Absorption spectroscopy describes the interaction between light and matter. As mentioned, when matter absorbs radiation, it causes electronic, vibrational, and rotational transitions (excitations). Light is absorbed only if the energy of the absorbed photon matches the difference between two quantised energy levels. This leads to dark lines in the spectrum known as an absorption spectrum, which is exclusive to the atomic and molecular makeup of the material being examined. After excitation, atoms and molecules can return to their ground state via two main pathways. Radiative relaxation occurs when the excited species emits a photon whose energy matches the energy difference between the excited state and the final state after relaxation. The wavelength of the emitted radiation is characteristic of the energy difference involved. Non-radiative relaxation involves the dissipation of excess energy through collisions with surrounding molecules, ultimately converting it into thermal energy. This mechanism is particularly relevant for vibrational relaxation, where the energy difference between vibrational states is typically smaller compared to electronic transitions.

2.1.8. Photophysical Processes

Molecules are usually in their lowest energy state, which is called the ground state, until they absorb energy, usually in the form of light. When this happens, an electron is excited, and it moves to a higher energy orbital. This results in the formation of an excited state. Even though these excited states usually exist for a very short time $(10^{-6} \text{ seconds})$, they play important roles in various phenomena such as photochemistry and electronics.¹¹ There are several mechanisms by which excited states can arise. In the case of atoms and molecules, such states can be triggered by the absorption of light, which prompts electrons to transition to higher energy orbitals. In solids, exciting vibrational or electronic modes can also generate excited states. Additionally, collisions with other particles can transfer energy to a system, facilitating its transition to an excited state. During chemical reactions, molecules frequently undergo intermediate excited states as they reconfigure their atoms and bonds.

Molecules in an excited state can be classified into two primary types: singlet and triplet states. The classification is based on the electron spin configuration. In singlet states, electrons have opposite spins, resulting in lower energy and a spin multiplicity of 1. Triplet states, on the other hand, possess electrons with parallel spins, which leads to higher energy due to spin-spin repulsion and a spin multiplicity of 3. These electron spin states are critical in understanding the reactivity of molecules and their interactions with other molecules.

2.1.8.1. Decay of Excited States

When an atom or molecule in an excited state moves to a lower energy state, it undergoes a process known as decay. The type of excited state and system determine the various forms of radiation or other processes through which energy is released during the transitions depicted in Figure 2.3.

Excited states can follow different pathways to decay, depending on their type and the system. The most common type of decay is radiation emission, where the system releases energy as electromagnetic radiation, such as photons. The frequency or wavelength of the emitted radiation corresponds to the energy difference between the initial and final states. Examples of radiation emission include fluorescence, phosphorescence, and blackbody radiation.





Figure 2.3. Simplified Jablonski Diagram of Photophysical Processes.

Non-radiative decay is another pathway for excited states to decay, where energy is lost through internal conversion, intermolecular quenching, or chemical reactions. The excited state can trigger chemical reactions, releasing energy as thermal energy or forming new chemical bonds.

Several factors, such as energy difference, selection rules, the nature of the excited state, and the environment, impact the rate of decay of an excited state. A larger energy difference leads to a faster decay rate. Excited states with different lifetimes exist, with short-lived states often decaying through non-radiative pathways and long-lived states having more radiative decay options.

2.1.8.2. Fluorescence

Fluorescence is a well-known optical phenomenon in which an atom or molecule is excited by absorbing light of a certain wavelength and subsequently emits radiation of the same or lower frequency within a brief duration of approximately 10^{-8} seconds. This emission is a result of a transition from a singlet excited state to the ground state of the atom or molecule. Fluorescent substances exhibit this phenomenon under sunlight containing ultraviolet photons (Figure 2.3).

 $S_1 \longrightarrow S_0$

2.1.8.3. Phosphorescence

Phosphorescence is a phenomenon that occurs when a molecule or atom absorbs high-frequency radiation, leading to the excitation of electrons. Unlike fluorescence, where the emission of radiation happens almost immediately, phosphorescence involves a delayed emission. This delay occurs because the excited electrons transition from the triplet excited state (T_1) to the ground state (S_0) , a

process that is less probable and thus slower. As a result, the material continues to emit radiation even after the incident radiation has stopped. This characteristic of phosphorescence finds applications in various fields, such as in glow-in-the-dark materials and in the study of molecular structures and dynamics. This transition is considered a forbidden transition and occurs at a slow rate; this is shown in Figure 2.3.

$$T_1 \longrightarrow S_0$$

The substance that displays this phenomenon is referred to as a phosphorescent substance. Phosphorescent materials have practical applications in objects such as luminous clock dials, as they can glow in the dark.

2.1.9. Stimulated and spontaneous processes

2.1.9.1. Spontaneous Absorption

Stimulated absorption is a process where an external electromagnetic field with the exact energy matching the energy difference between two energy levels in a material stimulates a constituent already in the lower energy state to absorb another photon and reach the higher energy level. This applies to atoms, molecules, or any entities within the material that possess quantised energy states. The absorption rate is proportional to both the intensity of the light and the concentration of molecules in the ground state. The equation provided, however, does not explicitly include these factors.^{8,13}

$$r = B\rho \tag{2.10}$$

Where *B* is the Einstein coefficient for stimulated absorption, which quantifies the probability of stimulated absorption, In Equation (2.10) ρ is the Planck distribution and *w* represents the rate of change of the probability of finding a molecule in the upper energy state after a stimulated absorption event. The Planck distribution also referred to as the Planck radiation law, defines the spectral density of electromagnetic radiation emitted by a black body in thermal equilibrium at a specific temperature. It depicts the energy distribution of photons emitted at different wavelengths or frequencies based on the body's temperature.¹³

W

2.1.9.2. Stimulated emission

The phenomenon of stimulated emission involves an excited molecule that interacts with a photon of light, which leads to the molecule emitting another photon. Two important features characterise this process. Firstly, the incident photon functions as a trigger, prompting the excited molecule to release its surplus energy as a new photon. However, the incident photon itself does not get consumed in the process. Secondly, the emitted photon has the same frequency and phase as the stimulating photon, resulting in highly coherent light. This principle underpins the functioning of lasers. The rate of stimulated emission can be attributed to two factors: the intensity of light and the concentration of excited molecules. A higher intensity of light, meaning more photons, can increase the probability of stimulating excited molecules to emit photons. Moreover, the likelihood of incident photons interacting with excited molecules and triggering stimulated emission is directly proportional to the concentration of excited molecules present.^{8,13}

$$w' = B' \rho \tag{2.11}$$

Where B' is the Einstein coefficient of stimulated emission (B and B' turn out to be the same for a 2-level system).

Lasers utilise stimulated emission to generate light with a precise frequency and phase.

2.1.9.3. Spontaneous emission

Spontaneous emission is a phenomenon where an excited atom or molecule releases a photon without any external influence. This process is independent of the intensity of the surrounding radiation. Einstein developed the Einstein *A* coefficient to describe the rate of spontaneous emission,

which represents the probability of this emission occurring per unit time. The overall emission rate from an excited state is the sum of both stimulated and spontaneous emission rates.

During spontaneous emission, the emitted photon has an energy equal to the energy difference between the excited and ground states, resulting in a specific frequency of light. The rate of spontaneous emission is proportional to the concentration of molecules in the excited state, meaning more excited molecules lead to a higher emission rate.^{8,13}

$$w' = (A + B')\rho$$
 (2.12)

where A is the Einstein coefficient of spontaneous emission.

2.1.10. Lasers: Light Amplification by Stimulated Emission of Radiation

Lasers have had a significant impact on both the field of chemistry and our daily lives. The operation of lasers depends on various optics and solid-state processes. Driven by stimulated emission, lasers operate when more than two electronic energy levels are involved, and an excited state emits a photon through radiation of the same frequency and phase as the stimulating photon. While the probability of a single atom emitting a photon at a specific frequency remains constant for a particular material, the overall emission rate increases with the number of photons present. This is because more photons present at the appropriate frequency translate to a higher chance of them triggering stimulated emission in excited atoms. This sets the stage for the crucial aspect of lasers - positive feedback.¹³

Lasers are categorised into four classes: Class I, Class II, Class III, and Class IV, based on the number of energy levels involved in achieving population inversion. Each class has different configurations and efficiency levels for various applications. Class I lasers operate with particles transitioning between two energy levels. However, achieving population inversion in a two-level system is particularly challenging, which limits the practicality of these lasers for most applications. Class II lasers, which involve a third energy level for population inversion, present a significant challenge. Particles are initially pumped to an excited state and then decay to an intermediate state, from which the laser transition occurs. Achieving population inversion in three-level lasers is difficult due to the substantial number of particles required to be in the excited state. Class III lasers facilitate population inversion by stimulating particles from the ground state to an excited state, followed by a transition to a metastable state. Population inversion occurs in this metastable state, making maintenance easier. Class IV lasers, which involve more than four energy levels, are utilised in complex laser systems to provide greater control over the laser transition and optimise performance.¹⁴

In a system, particles naturally move toward a state of minimum energy, where the number of particles in the lowest energy state is maximised (thermal equilibrium). However, in lasers, this tendency is counteracted; atoms usually tend to move towards the lower energy state due to thermal energy. Laser action necessitates the existence of a long-lived excited state, with a sufficiently long lifetime to participate in stimulated emission. Additionally, a crucial condition is that this long-lived state must have a greater population than the lower energy state where the transition terminates. This population difference facilitates net radiation emission. However, under thermal equilibrium, the situation is reversed. To achieve population inversion, i.e., to have more particles in the upper state than in the lower state, the matter is excited to an intermediate state I, which then changes into a lower state A by giving up some of its energy. The laser transition is the return of A to the ground state X (Figure 2.4). This arrangement leads to a three-level laser because three energy levels are involved overall. The process of pumping is when the $X \rightarrow I$ transition is stimulated with an intense flash of light or achieved with an electric discharge.¹³

The process of converting from I to A must occur fast, while the transition from A to X should be relatively gradual or just longer than $I \rightarrow A$. However, achieving population inversion with a three-level laser is difficult due to the high number of ground-state molecules that need to be converted to the excited state through pumping, suggesting that population inversion only happens after a

threshold is reached. To facilitate this process, a four-level laser configuration is utilised in which the laser transition culminates in a distinctive state A 'that differs from the ground state (Figure 2.4 (b)).

In a four-level laser system, achieving population inversion is easier compared to a three-level system. The lower energy state of the laser transition in a four-level system is not the ground state but a higher energy level. This results in a rapid decay of particles to the ground state after the laser transition, eliminating the need to pump a significant number of particles from the ground state as required in a three-level system. This characteristic simplifies the maintenance of population inversion in a four-level configuration.





(a) Class III laser, Stimulated emission transition (b $A \rightarrow X$ ar

(b) Class IV laser, population inversion between ${\cal A}$ and ${\cal A}'$



As A' is initially unoccupied, any occupancy in A results in a population inversion between A and A'. A crucial factor for achieving lasing in a four-level laser system hinges on the properties of state A. This state needs to be metastable, meaning it has a longer lifetime compared to the relaxation time from the upper excited state to A'. Furthermore, this population inversion can only be sustained if the $A' \rightarrow X$ transitions occur rapidly. Solid-state lasers typically use rare-earth element-doped crystals or glasses as their gain medium, and gas lasers utilise gases, such as helium-neon lasers or CO₂ lasers.¹³

2.1.12. Pi (π) and sigma (σ) orbitals

Electronic excitations or transitions can involve different types of orbitals, such as n, σ or π electrons. N (n) orbitals refer to nonbonding orbitals, or unshared electrons that reside in lone pair orbitals. Sigma (σ) orbitals are formed by overlap of s orbitals or sp, sp² or sp³ hybridised orbitals head-to-head along the bond axis, forming single bonds. Electron density for σ bonds exhibits circular symmetry around the bond axis. Pi (π) orbitals arise from the overlap of p atomic orbitals above and below the σ bond axis, forming double and triple bonds.

In addition to bonding orbitals, there are also anti-bonding orbitals. These orbitals have higher energy than bonding orbitals and can lead to molecular instability. For example, in a π bond, there is a bonding pi orbital and an anti-bonding π^* orbital. When an electron is promoted from the bonding pi orbital to the anti-bonding π^* orbital, it weakens the pi bond. The orbital involved in an electronic transition can affect the energy required for the transition and the properties of the excited state. For example, transitions involving n orbitals typically require lower energy than transitions involving σ or π orbitals. Transitions involving π orbitals often lead to the formation of coloured compounds.

Conjugation extends π systems across multiple bonds, lowering the energy gap between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO). This reduced energy gap makes the excitation of electrons in conjugated double bonds easier (lower energy required) compared to isolated double bonds, as evident in their UV/VIS spectra.



Figure 2.5. Generic Energy Level Diagram of a Molecule, Showing Bonding, Non-Bonding and Anti-Bonding Orbitals.

 $\pi \to \pi^*$ involve the promotion of an electron from a bonding π orbital to an antibonding π^* orbital, typically resulting in the absorption of light in the ultraviolet or visible region of the spectrum. Transitions involving electrons moving from non-bonding n orbitals to antibonding π * orbitals ($n \to \pi^*$) have lower energies than $n \to \sigma^*$ transitions due to the lower energy of π^* orbitals compared to σ^* orbitals. Transitions from $n \to \pi^*$ or $n \to \sigma^*$ are significantly less intense (molar absorptivity) compared to $\pi \to \pi^*$ or $\sigma \to \sigma^*$ transitions. This is because n orbitals have spatial orientations that violate selection rules, making these transitions forbidden or less probable.

2.1.13. Photoinduced Processes in Semimetals, Metals and Semiconductors

2.1.13.1. Metals

In Chapter 1, it was mentioned that metals can conduct electricity well because of their overlapping valence and conduction bands. This allows for many delocalised electrons to move easily and carry current. Metals also have a high carrier density, meaning they have many free electrons that respond to light and participate in photochemical processes. When light excites electrons from the valence band, they can move to higher energy levels within the conduction band or escape the metal altogether. This process, known as intra-band and inter-band transitions, can result in "hot electrons" with high kinetic energy capable of breaking bonds or driving reactions. Nanostructured metals can also support surface plasmon resonance, similar to semimetals, which can lead to localised energy concentrations for plasmon-driven chemistry. However, the high density of free electrons and fast relaxation processes can make it challenging to control and utilise photogenerated carriers effectively for specific reactions. As temperature increases, the conductivity of metals generally decreases slightly due to increased resistance caused by electron-phonon scattering.

Interestingly, all zigzag graphene nanoribbons, regardless of width, exhibit metallic behaviour due to their unique electronic structure at the edges, which leads to delocalised states along the ribbon.¹⁵

2.1.13.2. Semimetals

Semimetals are a remarkable class of materials with distinct characteristics that set them apart from semiconductors. Their valence and conduction bands overlap, meaning that free carriers are present even without light excitation, which affects their response to light. Semimetals can be excited by light in various ways, including direct band-to-band transitions, intra-band transitions, and surface plasmon

resonance. As a result, semimetals exhibit complex carrier dynamics compared to semiconductors. Photogenerated carriers participate in various reactions, including direct bond breaking and charge transfer, depending on the material and environment.

Semimetals also have notable electrical conductivity values due to an extremely small or even no band gap, leading to the conductivities between those of metals and semiconductors. At room temperature, they exhibit metallic behaviour, but they can display semiconductor-like properties at lower temperatures. Examples of semimetals include bismuth, antimony, and graphene. Their conduction and valence bands have minimal or no separation, resulting in a partially filled conduction band at room temperature. Semimetals have an intermediate concentration of free electrons compared to metals and intrinsic semiconductors.

2.1.13.3. Semiconductors

The gap between the filled valence band and empty conduction band of semiconductors limits the movement of electrons and results in a low concentration of free electrons in their natural state. However, by introducing heat, light, or impurities, known as doping, electrons can be excited across the band gap, enabling conductivity.

The band gap plays a vital role in photochemistry, dictating the necessary light energy to excite electrons and enable conductivity. When light with energy equal to or exceeding the band gap interacts with the semiconductor, it promotes electrons from the valence band to the conduction band, forming electron-hole pairs. The wavelength of the light impacts the number and energy of the excited carriers, influencing the reaction pathways. Efficiency in separating and transporting these electron-hole pairs to reaction sites is critical for effective photochemical conversion.

Functionalised Graphene is a form of graphene-based semiconductor that involves attaching specific functional groups to graphene to modify its electronic properties and induce semiconducting behaviour. The addition of different functional groups can create bandgaps with diverse characteristics, such as graphene oxide. Additionally, armchair graphene nanoribbons fall under the category of semiconductors. These materials are widely utilised in electronic applications, such as transistors and solar cells, where their controllable conductivity is leveraged.¹⁶

2.1.13.4. Processes in Solids

Phonons

Phonons are quasiparticles representing the quantisation of lattice vibrations. Depending on the specific vibration patterns, phonons can be categorised into two types, such as acoustic phonons and optical phonons. Although not fundamental particles, phonons exhibit behaviour similar to massless bosons, meaning they can be created or destroyed with minimal energy input. Additionally, their energy distribution resembles that of a blackbody, with their peak energy aligning with the material's temperature.

Electron-phonon scattering

When electrons move freely within a vibrating lattice, their interactions with phonons can lead to electron-phonon scattering. This scattering process significantly impacts various material properties. The scattering can be either elastic or inelastic. Elastic scattering refers to the scenario where the electron bounces off a phonon, conserving its total energy. In inelastic scattering, the electron absorbs or emits a phonon, resulting in a change in the electron's energy. Electron-phonon scattering disrupts the flow of electrons, causing increased electrical resistance. It also reduces thermal conductivity. However, under specific conditions at very low temperatures, electron-phonon coupling can facilitate superconductivity, where electrical resistance vanishes entirely.¹⁷

Electron-electron scattering

The phenomenon of electron-electron scattering applies to electrons interacting directly with each other, which occurs due to their inherent Coulombic repulsion. Electron-electron scattering is classified into two types, intra-band scattering, where electrons scatter within the same energy band, and inter-band scattering, where electrons scatter between different energy bands.

Several factors influence electron-electron scattering, including electron density, which leads to more frequent collisions and stronger scattering with higher electron density. Electrons with higher energy experience a stronger repulsive force, resulting in more pronounced scattering.

Charge Transfer

Charge transfer is the process by which electrons move between atoms, molecules, or solids. This movement can involve a complete transfer of an electron from one entity to another or a partial transfer, resulting in the sharing or delocalisation of electron density across multiple atoms. Delocalisation creates a material with a more spread-out electron cloud, influencing its chemical properties.

When a molecule absorbs light, it can excite an electron from a π orbital into an antibonding π^* orbital. As mentioned before, this is known as a $\pi^* \leftarrow \pi$ transition. The energy of this transition is approximately 7 eV for an unconjugated double bond, corresponding to an absorption at 180 nm in the ultraviolet. If the double bond is part of a conjugated chain, the molecular orbitals lie closer together, causing the $\pi^* \leftarrow \pi$ transition to move to longer wavelengths. In some cases, it may even lie in the visible region if the conjugated system is big enough.

2.2. SPECTROSCOPY

Spectroscopy is a scientific discipline that explores the interactions between light and other forms of radiation with matter, providing insights into its composition and structure. By utilising a combination of spectroscopic techniques, including emission and absorption spectroscopy, a thorough and comprehensive characterisation of graphene-based films can be achieved. This integrated approach provides a multifaceted investigation, revealing the elemental composition, chemical functionalities, bandgaps, and carrier processes of the samples.

Within this field, photoemission spectroscopy involves measuring the kinetic energy and the number of electrons released from a material when exposed to light or X-rays. On the other hand, absorption spectroscopy examines the extent to which a material absorbs radiation as a function of its wavelength. Absorption spectroscopy involves studying the radiation spectrum to uncover important details about the properties of the matter under investigation, employing light as a tool to probe matter. The relationship between absorbance (A) and transmittance (T) is inversely proportional and logarithmic.

$$A = -log(T) \tag{2.13}$$

Transmittance is the fraction of light that passes through a sample at a specific frequency. The Beer-Lambert law (Equation (2.7)) relates transmittance to sample length (l) and concentration of absorbing species (c), through the molar absorption coefficient (ε) The Beer-Lambert law can also be written as:

$$I = I_0 \times 10^{(-\varepsilon[c]l)} \tag{2.14}$$

Where I=Transmitted intensity and I_0 = Incident intensity

2.2.1. Atomic Spectroscopy

When electromagnetic radiation interacts with atoms, phenomena investigated by atomic spectroscopy emerge. Analysis of the radiation emitted or absorbed by atoms reveals valuable insights into their unique structure and energy levels; each element possesses distinct energy levels for its electrons, which become observable during the interaction with radiation. When photons with sufficient energy are absorbed, the atom jumps to a higher energy level, creating a specific atomic absorption spectrum. Similarly, when an excited atom returns to its ground state, it emits energy in the form of a photon with a specific wavelength, producing an atomic emission spectrum that reveals details about the atom's transitions and excited states. The lines in the spectrum occur when the atom undergoes a transition with a change of energy (ΔE) and emits or absorbs a photon of frequency $\nu = (\Delta E)/h$ and $\bar{v} = (\Delta E)/hc$, however, electron-electron interactions and additional energy contributions complicate direct translation of the spectrum into individual orbital energies.¹³

Atomic spectroscopy has a variety of applications, such as identifying and quantifying elements in a sample, understanding the energy levels and electronic configurations of elements, and understanding the excited states involved in chemical processes.

2.2.2. Molecular Spectroscopy

Molecular spectroscopy is the study of molecules with various vibrational and rotational modes, in addition to electronic transitions like in atoms. When electromagnetic radiation interacts with molecules, they absorb radiation and get excited from the ground state energy level to another level (electronic, vibrationally, or rotationally excited). The origin of spectral lines in molecular spectroscopy is the absorption, emission, or scattering of a photon when the energy of a molecule changes; these complex molecular spectra can reveal useful information about the molecular structure, stability, and other characteristics, such as bond lengths, angles, functional groups, and vibrational frequencies that aid in identification. Furthermore, studying how molecules vibrate, rotate, and undergo transitions provides insights into their chemical dynamics and behaviour.¹³

Applications of molecular spectroscopy include identifying unknown compounds by matching measured spectra with reference databases and studying chemical reactions by monitoring changes.

2.3. SPECTROSCOPY TECHNIQUES

2.3.1. Ultraviolet-Visible Spectroscopy

UV-visible (UV-vis) spectroscopy is an incredibly versatile analytical technique that has been utilised in a variety of contexts for both qualitative and quantitative analysis, online reaction monitoring, and structure determination across a diverse range of environments. Its applications are extensive, covering a broad scope of materials and compounds. UV-vis spectroscopy can provide a wealth of information, including structural and electronic details, depending on the structure of the compound being studied. As a result, researchers frequently rely on UV-vis spectroscopy to analyse various materials and compounds.¹⁸

UV-Vis spectrophotometers use a light source to illuminate a sample with light in the UV to visible wavelength range, typically from 200 to 800 nm. These spectrophotometers measure the amount of light absorbed, transmitted, or reflected by the sample at each wavelength. Some spectrophotometers have an extended wavelength range that goes into the near-infrared (NIR) range, from 800 to 3200 nm.

UV-vis spectrophotometers rely on the monochromator to filter and direct light precisely onto the sample being studied. The monochromator acts as a wavelength filter, allowing only a specific range of wavelengths to interact with the sample. By scanning different wavelengths, a complete spectrum will be obtained, that reveals how the sample interacts with light at various energy levels. The prism monochromator uses the refraction properties of a prism to isolate and direct the desired wavelength through a slit. The grating monochromator uses a diffraction grating to diffract light based on its wavelength and focus it through the slit.

The resolution of the monochromator determines the narrowness of the selected wavelength range. The higher the resolution, the more precise measurements and differentiation between closely spaced peaks. The width of the slit can control the amount of light passing through the monochromator; a narrower slit provides higher resolution but less intensity. The monochromator is depicted in Figure 2.6, showing the schematic diagram of a UV-Vis spectrophotometer.




UV-Vis spectroscopy has proven to be a valuable technique for studying graphene films. UV-Vis spectra can detect the presence of defects or impurities in the graphene film. These imperfections are characterised by a difference in the absorption peak as compared to pure graphene. Moreover, the absorption profile can be altered by the presence of functional groups such as those found in aerogel graphene.¹⁹

2.3.2. Fourier Transform Infrared and Attenuated Total Reflectance

Fourier transforms are mathematical tools that enable the analysis of physical processes by converting between their serial (time/space) and spectral (frequency/energy) representations. They are particularly useful in spectroscopy as they offer a key advantage in that they enable faster measurements. In certain spectroscopic techniques, Fourier transforms can significantly accelerate data acquisition compared to traditional methods, and they are used to interpret data, improve resolution, and mimic natural processes like diffraction.²⁰

The concept behind Fourier transforms is that many physical phenomena can be described as combinations of simple periodic waves. It can be used to analyse both periodic and non-periodic signals. The availability of computers and efficient algorithms like the Fast Fourier Transform (FFT) has made them widely accessible. Fourier transforms offer significant advantages in terms of sensitivity, speed, and resolution compared to traditional methods and can also extract the true spectrum from data affected by limitations like slow detector response.²⁰

Fourier transform infrared (FTIR) is an analytical spectroscopic technique that uses the infrared (IR) range of the electromagnetic spectrum to assess the chemical composition of a sample. When IR radiation interacts with matter specific frequencies are absorbed, decreasing the intensity of the incident radiation. By analysing this absorption pattern, an IR spectrum is created, which acts as a distinctive identification of the sample. Infrared radiation includes wavelengths ranging from roughly 780 nm to 100 μ m, corresponding to frequencies of 12,800 cm⁻¹ to 100 cm⁻¹. Each vibrational or rovibrational mode of a molecule possesses a distinct energy level, which corresponds to a specific frequency in the infrared region of the electromagnetic spectrum.²¹

The FTIR instrument measures the intensity of the IR radiation at different frequencies to create a spectrum that shows absorption bands at frequencies corresponding to the vibrational modes of the molecules in the sample. The positions and intensities and of these bands depend on the specific bonds present and the sample concentrations.

Attenuated Total Reflectance (ATR) is the preferred sampling technique used with FTIR spectroscopy to analyse solids and films, without any preparation. An ATR crystal with a high refractive index is used to generate an evanescent wave that interacts with the molecules in the sample, leading to the absorption of IR radiation at their characteristic frequencies. ATR is non-destructive and can analyse various materials, including layered samples.²¹

FTIR and ATR are two of the spectroscopy techniques used to study the properties of graphene and aerogel graphene films. FTIR can identify the specific chemical bonds or functional groups present in the film, while ATR is particularly useful for studying thin films or surfaces. By analysing the surface layer of the graphene film, ATR can provide insights into potential contaminants or the presence of different functional groups.

2.3.4. Transient Absorption

Time-resolved spectroscopy is a pulsed-laser-based technique used to study ultrafast processes, meaning those occurring on incredibly short timescales, often ranging from femtoseconds (10^{-15} seconds) to picoseconds (10^{-12} seconds). It uses pulses of light as a probe to understand how materials change over time after being excited by another light source. Lasers, since their invention in 1960, have offered unparalleled ability to tailor light parameters, including intensity, wavelength, direction, pulse duration (measured in femtoseconds), polarisation, and phase.

Transient absorption spectroscopy (TAS) offers a powerful tool for unravelling the complex world of ultrafast electron dynamics in matter on femtosecond timescales. This technique relies on the interaction of a pump pulse and a probe pulse from two laser beams.

With its short duration and high intensity, the pump pulse excites a fraction of the sample from the ground state to the excited state. This initial excitation disrupts the equilibrium, prompting a flow of photophysical and photochemical responses within the system. The probe pulse arrives at a controlled time delay (τ) after the pump pulse, and its low intensity is low enough to ensure minimal perturbation and avoid undesired multiphoton processes. By measuring the change in absorbance (ΔA) at different wavelengths and time delays ($\Delta A(\lambda, \tau)$), TAS unveils the evolution of the excited state population and associated dynamics.²²

The $\Delta A(\lambda, \tau)$ profile is a useful source of information about a system's dynamics, as it provides insights into various processes, such as electron and/or proton transfer processes, excited-state energy migration, which refers to the transfer of excitation energy between various molecules or sites within a system, and intersystem crossing, which is the transition between singlet and triplet excited states.

Compared to time-resolved fluorescence, TAS offers a distinct advantage. By probing changes in absorption, it can reveal the evolution of non-emissive and dark states, which are often crucial in complex systems, such as photosystems where non-emissive carotenoid states play vital roles. Advanced global analysis techniques are often employed to fully extract the rich information encoded in $\Delta A(\lambda, \tau)$. These methods allow for the simultaneous fitting of the entire dataset, leading to a deeper understanding of the underlying dynamics, extraction of kinetic constants and mechanistic insights.²²

During transient absorption experiments, a ground state absorption spectrum acquired via the probe (hv_{probe}) , is compared to the absorption after excitation by a pump (hv_{pump}) , leading to a differential absorption spectrum, ΔA . Data are typically reported either in terms of changes in absorbance or in transmittance. Absorbance is on a logarithmic scale, while transmittance is on a linear scale. For example, an absorbance of 1 equals a transmittance of 10%.

$$T = \frac{P}{P_0} \tag{2.15}$$

$$A = -\log \frac{P}{P_0} \tag{2.16}$$

where T- transmittance (how much light passed through), P- power out (the amount of power sent to the sample), P_0 - power in and A- absorbance.

$$\Delta T$$
 is converted into ΔA using the following equation (2.17):

$$\Delta A = -\log(\Delta T + 1)$$
(2.17)

$$A(t) - A(0) = \Delta A \tag{2.18}$$

where A(t) = absorbance at time t after laser pulse and A(0) = absorbance without laser pulse.

$$\Delta A = \Delta A(t,\lambda) \tag{2.19}$$

To record the probe's transmission, it needs to be measured both with and without the initial excitation. This can be achieved by modulating the pump's repetition rate through a chopper, either mechanical or optical. The change in transmission can then be calculated.

$$\Delta T = \frac{(T^* - T)}{T} \tag{2.20}$$

 T^* = transmission of the probe through the pumped sample and T = transmission of the probe through the un-pumped sample

2.3.4.1. Analysis of Pump-Probe Data

In TA, the change in absorbance of the sample is collected as a function of pump-probe delay (t) and probe wavelength (λ). The data obtained by the spectroscopy technique, $\Delta A(t, \lambda)$, is presented as a matrix, where a column of the table is the differential spectrum at a given delay time (known as a time-gated spectrum) and a row is the kinetic trace at a given wavelength (change in ΔA as a function of t).

2.3.4.2. ∆A Spectrum

The primary focus of information gained from the ΔA spectrum is on key signals such as ground state bleaching, stimulated emission, and excited state absorption. While other phenomena, like multiphoton processes, molecular reactions, and ionisation, can contribute to the ΔA spectrum, they are not focused on here as they are considered background noise for most applications.

Figures 2.7 and 2.8 illustrate the various processes occurring during transient absorption spectroscopy and their contributions to the transient signal for solid-state materials and molecules, respectively.



Figure 2.7. Schematic of the Various Photoinduced Processes in a Solid and their Contribution to the Transient Signal: electron and hole absorption (EA, HA), ground state bleach (GSB), and stimulated emission (SE).



Figure 2.8. (a) Simplified Energy Level Scheme Depicting the Various Electronic Transitions of a Molecular System, (b) Transient Absorption Difference Spectrum Decomposed into GSB, ESA and SE contributions. The dashed line is the sum of these contributions. ESA= Excited state absorption, GSB= Ground state bleach, SE= simulated emission, S_0 = ground electronic state, S_n = excited and S_{n+1} = transient state.

Ground-State Bleach (GSB)

GSB reflects the depopulation of the ground state due to excitation by the pump pulse. In TA, molecules in the ground state absorb light at specific wavelengths, creating the "ground state absorption" spectrum. When these molecules get excited, they can no longer absorb light at those same wavelengths, leading to a decrease in absorption compared to the original ground state. This decrease appears as a negative signal in the TA spectrum, shown in Figure 2.7.

Stimulated Emission (SE)

Stimulated Emission arises in solid-state materials and molecules when the probe pulse interacts with an excited state created by the pump pulse. This interaction "stimulates" the excited state to emit light at the same wavelength as the incoming probe pulse. The emitted light contributes to the TA signal, resulting in a negative peak similar to fluorescence. However, unlike fluorescence, SE exhibits a *red shift* with a longer wavelength compared to the GSB peak. This phenomenon (known as a Stokes shift, when considering molecules) occurs because the excited electronic state undergoes vibrational relaxation after absorbing the pump pulse. This relaxation lowers the energy level of the excited state before it emits light via SE, leading to emission from a slightly lower energy level and a consequent red shift.

Excited-State Absorption

Excited state absorption contributes positively to the TA spectrum, arising when already excited molecules absorb the probing photon. This additional absorption propels these molecules to even higher energy states. The ESA peak location in the TA spectrum corresponds directly to the energy gap between the initially occupied excited state and the higher excited state reached after absorbing the probe photon.

Femtosecond pulsed lasers provide significant advantages for Pump-Probe spectroscopy when compared to other light sources. Femtosecond lasers achieve much narrower bandwidths compared to continuous wave (CW) lasers. This is because their energy is concentrated into incredibly short pulses, a principle governed by the Heisenberg uncertainty principle. A narrow bandwidth translates to high spectral selectivity. These lasers possess a wide range of usable wavelengths, typically infrared to ultraviolet. Femtosecond lasers have pulse durations in the femtosecond range, which can capture ultrafast dynamics occurring within molecules and materials. This feature is crucial for studying chemical reactions, electron transfer, and phonon interactions. Rapid data acquisition is ensured by high repetition rates, allowing researchers to collect data and build up signal-to-noise ratios even when studying low-probability events.



Transient Absorption Instrumental Set-Up

Figure 2.9. A simplified Schematic of a Pump-Probe Experiment

Figure 2.9 shows a simplified schematic of the pump-probe experiment, which is set up in the Lord Porter laser lab at the University of Sheffield. A Ti: sapphire regenerative amplifier generates 800 nm femtosecond pulses. A beam splitter separates the amplified output into pump and probe beams. The probe beam traverses a computer-controlled delay stage to adjust its arrival time at the sample relative to the pump beam.

The pump beam enters an optical parametric amplifier (OPA) (not shown in the scheme in Figure 2.9) enabling selective tuning of its frequency. A chopper (mechanical or optical) modulates the pump's pulse repetition rate, allowing probing of both pumped and unpumped samples. The 800 nm probe is focused into a crystal, as depicted, generating a single-point white light continuum. After passing through the sample, the light experiences spectral dispersion and is then coupled into an optical fibre cable for detection. This technique, often referred to as UV-Vis TA, relies on tuning both pump and probe beams to the system's electronic transition energies. By adjusting the probe's delay and the pump's frequency, researchers can probe ultrafast dynamics occurring in the sample upon photoexcitation.

Conventional spectroscopic techniques for material characterisation often lack the necessary temporal resolution to probe the ultrafast phenomena that govern material behaviour at the atomic level. Ultrafast transient absorption spectroscopy overcomes the limitations of traditional methods. Analysing the decay of excited states in graphene films with ultrafast laser spectroscopy allows for the extraction of key information about various material processes. Fitting the decay traces with exponential functions determines the rates and lifetimes of specific excited state processes relevant to graphene, including charge transfer, carrier-carrier scattering, carrier-phonon scattering, charge recombination, and trapped states due to doping or defects.

2.3.5. X-ray Photoelectron Spectroscopy

X-ray Photoelectron Spectroscopy (XPS) is a spectroscopic technique used to examine a sample's chemical composition by probing its electronic structure. This surface characterisation technique can analyse a sample to a depth of 2 to 5 nanometres. XPS is based on the photoelectric effect, discovered by Heinrich Hertz in 1887 and explained by Albert Einstein in 1905. While the technique's roots lie in earlier work, Physics Nobel Prize winner Kai Siegbahn's significant advancements in instrumentation

and interpretation in the 1950s and 1960s are credited with establishing XPS as a widely used analytical tool. $^{\rm 4.23.24}$

The procedure begins by irradiating a sample with an X-ray beam and quantifying the kinetic energy and the number of electrons ejected from the sample. X-rays or hard ultraviolet ionising radiation of energy in the range 5-40 eV can be used, giving rise to the XPS and UPS techniques, respectively. When the incident photon's energy is high enough, electrons are ejected from the inner cores of atoms, providing information about ionisation energies. Core ionisation energies are characteristic of the individual atom, but they can also be shifted slightly depending on the chemical state of the atom, a phenomenon known as chemical shift. Chemical shifts can reveal information about the types of bonds that are present in a sample. XPS enables the determination of the chemical composition of various materials. This technique is able to reveal what chemical elements are present on the surface, as well as give information about the nature of the bonds among the surface elements.

XPS is typically considered a non-destructive surface-sensitive method, which is useful for elemental mapping of unknown and known solids, and it provides quantitative measurements. As well as being a particularly effective and useful technique, it is, unfortunately, quite an expensive and time-consuming process that requires a high vacuum. One significant disadvantage of this method is that it cannot detect hydrogen or helium in a sample, as it can only detect any element with an atomic number higher than 3. Hydrogen has no inner shell electrons, so core–electron XPS is impossible. The H 1s electrons are valence electrons and participate in chemical bonding. Any signal present from hydrogen would overlap with signals from the excitation of valence electrons from other surface atoms.²⁵

During the XPS experiment, X-rays are fired onto the sample surface, resulting in electrons being emitted. The energy of the emitted electrons is used to calculate the composition of the sample. Auger electrons are detected during this process, and the kinetic energy of the electrons is represented on a screen, providing data on the sample's elements. Peaks in the spectrum appear from atoms emitting electrons of a particular energy, and the peak areas quantify the concentration of the present elements.²⁶

In this study, XPS was used to investigate the core electron binding energies of carbon and oxygen in the samples of graphene and AG. The study aimed to explore the differences in binding energies among the samples with single, bi, and tri-layers of graphene and AG. Additionally, the effect of increasing the oxygen content in the AG ink-printed films was observed and studied.

2.3.6. Raman Spectroscopy

Raman spectroscopy is a technique used to analyse vibrational energy levels of matter. It achieves this by investigating the frequencies of scattered light. It involves the use of several types of scattered light, each of which helps to provide a more complete understanding of the material properties. About one in 10⁷ incident photons collide with matter, give up some of their energy, and emerge with lower energy. These scattered photons are known as the lower-frequency Stokes radiation. Other photons may collect energy from the excited molecules and emerge as higher-frequency anti-Stokes radiation. The component of radiation scattered without a change in frequency is known as Rayleigh radiation. Raman spectroscopy focuses on the energy differences between the ground state and vibrational energy levels in molecules.¹³

Raman and FTIR are two analytical techniques that analyse the vibrational energies of samples. While Raman provides a unique and detailed characterisation of specific molecules, FTIR offers a broader view of functional groups. In this study, Raman spectroscopy was used to identify the differences between graphene and aerogel graphene film samples and to compare the reproducibility and consistency of AG samples made at different times.

2.4. OTHER CHARACTERISATION TECHNIQUES

In addition to utilising several spectroscopic techniques, this research also employed other techniques, such as electron microscopy, for a more detailed investigation of the morphology, particle size, layer arrangement, and thickness of the graphene-based printed ink samples.

2.4.1 Electron Microscopy

Electron microscopes were first developed in the 1930s and 40s. They provide a resolution 1000 times better than light microscopy and can magnify specimens up to 1,000,000 times. Electron microscopes use beams of electrons that can interact with the sample as the beam is transmitted through the sample. This immense magnification capability stems from the use of electrons instead of light.¹³

According to de Broglie's theory, particles, such as electrons, demonstrate wave-like characteristics. In comparison to visible light, electrons exhibit a significantly smaller de Broglie wavelength (around 0.01 nanometres). The shorter the wavelength, the more precise the instrument's resolution abilities become, enabling electron microscopes to visualise features that are thousands of times smaller than those visible through light microscopes.²⁷

2.4.2. Scanning Electron Microscopy

The scanning electron microscope (SEM) is a high-magnification imaging tool that utilises a focused electron beam to examine sample surfaces. As the beam interacts with the sample, it generates signals that reveal valuable information about the topography and composition of the surface. Similar to transmission electron microscopes, SEMs also relies on an electron beam. However, the imaging and visualisation of SEMs is based on secondary electron emission. When the beam scans the surface of the sample, it causes the ejection of secondary electrons. SEMs have two detection systems: the secondary electron detector and the backscatter electron detector. While the backscatter detector provides results for the magnetic fields and crystallography of the sample, the secondary electron detector enables visualisation of the topography. The electron signal is then converted into a light signal and amplified via a photomultiplier, resulting in an image projected onto a computer screen; SEMs can also provide 3D images.²⁸ A simple schematic of SEM is displayed in Figure 2.10. SEM was used in this research, to visualise the variations in particle size of graphene aerogel with varying oxygen content.



Figure 2.10. Schematic of SEM drawn using PowerPoint.

2.4.3. Transmission Electron Microscopy

The Transmission Electron Microscope (TEM) was developed as a solution to the limited image resolutions offered by light microscopes, which were restricted by the wavelength of visible light. After the de Broglie wavelength discovery in 1927, Davisson and Germer conducted their electrondiffraction experiments, which displayed the wave nature of electrons.²⁹ These findings allowed Ruska to take the first-ever electron microscope images in 1932. He later suggested the theory for electron microscopes, for which he won a Nobel prize in 1986.³⁰

In TEM, samples are fixed onto a supported grid, either after being stained using compounds such as uranyl acetate or put into place as they are. Accelerated electrons then pass through the specimen, and regions on the sample can be dense or sparse based on how many electrons they scatter. When an area on the sample scatters more electrons, it is called an electron-dense region. If electrons pass through the electron-dense regions, they will lose more energy compared to the sparse regions. TEM uses this procedure to visualise the sample at a high level of resolution and magnification. Samples for TEM are cut into ultra-thin slices using a diamond knife so that the electrons are able to pass through them.³¹

Once the sample is set up in a TEM arrangement, the electron gun shoots an electron beam through the anode. The electron beam passes through the sample and loses energy in the electron dense region. Then it goes into the objective lens, which can magnify the image. The electrons pass through the projector, or ocular lens, which can magnify it further. Finally, the beam is transmitted to the fluorescent screen, where it is interpreted as an image that is recorded and displayed. A simple schematic of the TEM set up is shown in Figure 2.11.

TEM can display various characteristics of the sample, such as morphology, crystallisation, stress, and even magnetic domains. Its resolution can be below 0.05 nanometres. TEM was utilised in this PhD project to investigate the arrangement of graphene-based structures in the film samples and to distinguish the morphology differences between pure graphene films and aerogel graphene films.



Figure 2.11. Schematic of TEM drawn using PowerPoint

2.4.4. Atomic Force Microscopy

Atomic force microscopy (AFM) uses a very small probe to measure forces between the probe and the sample surface at high resolution. This technique offers information about surface topography and adhesion forces. In AFM, a sharpened tip attached to a cantilever is scanned across the surface. The force exerted by the surface and any bound species attracts or repels the tip, which in turn deflects the cantilever. The deflection is monitored either by interferometry or by using a laser beam. This study employed AFM to determine the thickness of some of the graphene-based films. The investigation involved evaluating the thickness of films generated using varying numbers of printed passes and varying oxygen content. The study aimed to explore the correlation between these parameters and the graphene film thickness.

2.4.5. Scanning Near-Field Optical Microscopy

Scanning Near-Field Optical Microscopy (SNOM) is an advanced optical technique that surpasses the diffraction limit, enabling high-resolution imaging and spectroscopy on the nanoscale. This method combines the principles of AFM with optical measurements to acquire topographical and optical information from the sample. Typically, a sharp metallic tip is illuminated with incident light, which is then scattered by the tip as it interacts with the sample surface. The scattered light contains near-field contributions that provide optical data with resolutions below 20 nm.^{32,33}

In SNOM, the polarizability of the metallic tip, which is influenced by the sample's local dielectric environment, plays a crucial role. The electronic, vibrational, or phonon resonances of the tip and the sample can affect their interaction. These interactions alter the scattered light, enabling SNOM to detect changes in optical absorption with high spatial precision.

This study employed a combined SNOM and AFM approach to investigate the presence of carbonoxygen functional groups within the AG films through vibrational spectroscopy.

2.4.6. Profilometry: Optical Surface Analysis

Profilometry is a method employed for the analysis of surface microtopography. The optical profiler utilised for this purpose is the Bruker ContourGT-I,³⁴ which employs light to generate highly detailed maps of surface features. Equipped with a fully motorised XY stage and tip/tilt head, this system facilitates precise surface measurements. Importantly, profilometry is a non-destructive technique, ensuring the integrity of the samples during analysis.

The Bruker ContourGT-I is an extremely versatile instrument capable of analysing a wide variety of materials and surface types. Its high precision makes it well-suited for measuring even the most minute surface details. With a vertical resolution of up to 0.01 nm, the instrument's capabilities are comparable to those of advanced microscopy techniques such as TEM. To ensure accurate measurements, it is essential to minimise external vibrations and noise, as these factors can significantly impact the quality of the surface maps.

In this study, a profilometer was employed to investigate the thickness of specimens that were too large to be accommodated in the available AFM setup. Additionally, it was utilised to examine the evenness of the printed passes of graphene-based ink on the quartz surface of the specimens.

2.5. REFERENCES

¹ Petr Klán, & Wirz, J. (2009). *Photochemistry of Organic Compounds*. John Wiley & Sons.

² Platt, U., Stutz, J., & Springerlink (Online Service. (2008). *Differential Optical Absorption Spectroscopy : Principles and Applications*. Springer Berlin Heidelberg.

³ Maxwell, J. (1865). VIII. A dynamical theory of the electromagnetic field. *Philosophical Transactions of the Royal Society of London*, 155, 459–512. <u>https://doi.org/10.1098/rstl.1865.0008</u>

⁴ Hertz, H. G., & Doncel, M. G. (1995). Heinrich Hertz's laboratory notes of 1887. *Archive for History of Exact Sciences*, *49*(3), 197–270. <u>https://doi.org/10.1007/bf00376092</u>

⁵ Balmer, J. J. (1885). Notiz über die Spectrallinien des Wasserstoffs. *Annalen Der Physik*, 261(5), 80–87. https://doi.org/10.1002/andp.18852610506

⁶ Rydberg, J. R. (1890). XXXIV. On the structure of the line-spectra of the chemical elements. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science*, *29*(179), 331–337. https://doi.org/10.1080/14786449008619945

⁷ Lyman, T. (1906). The Spectrum of Hydrogen in the Region of Extremely Short Wave-Length. *Memoirs of the American Academy of Arts and Sciences*, 13(3), 125. <u>https://doi.org/10.2307/25058084</u>

⁸ Serway, R. A., & Jewett, J. W. (2007). Physics for Scientists and Engineers with Modern Physics. Brooks/Cole Publishing Company.

⁹ Planck, M. (1901). Ueber das Gesetz der Energieverteilung im Normalspectrum. *Annalen Der Physik*, 309(3), 553–563. <u>https://doi.org/10.1002/andp.19013090310</u>

¹⁰ Qasim, M. *Simplified Concepts in Spectroscopy and Photochemistry*; U.S. Army Engineer Waterways Experiment Station, 1997.

¹¹ Singh, N. B., Shiva Saran Das, & Singh, A. K. (2009). *Physical chemistry. volume II*. New Age International.

¹² Atkins, P. W., Julio De Paula, & Keeler, J. (2018). *Atkins' physical chemistry* (11th ed.). Oxford University Press.

¹³ Atkins, P. W., & de Paula, J. (2006). *Physical Chemistry*. W.H. Freeman.

¹⁴ Svelto, O. (2010). *Principles of Lasers*. Springer US. <u>https://doi.org/10.1007/978-1-4419-1302-9</u>

¹⁵ Warner, J. H., Schaffel, F., Rummeli, M., & Alicja Bachmatiuk. (2012). *Graphene*. Newnes.

¹⁶ Ramalingam, G., Perumal, N., Priya, A. K., & Rajendran, S. (2022). A review of graphene-based semiconductors for photocatalytic degradation of pollutants in wastewater. *Chemosphere*, *300*, 134391. https://doi.org/10.1016/j.chemosphere.2022.134391

¹⁷ Zhong, Y., Li, S., Liu, H., Dong, Y., Aido, K., Arai, Y., Li, H., Zhang, W., Shi, Y., Wang, Z., Shin, S., N, L. H., Miao, H., Kondo, T., & Okazaki, K. (2023). Testing electron–phonon coupling for the superconductivity in kagome metal CsV3Sb5. *Nature Communications*, *14*(1). <u>https://doi.org/10.1038/s41467-023-37605-7</u>

¹⁸ Lindon, J. C., Koppenaal, D. W., & Tranter, G. E. (2016). *Encyclopedia of Spectroscopy and Spectrometry*. San Diego Elsevier Science & Technology Ann Arbor, Michigan Proquest.

¹⁹ Xu, Y., Sheng, K., Li, C., & Shi, G. (2010). Self-Assembled Graphene Hydrogel via a One-Step Hydrothermal Process. ACS Nano, 4(7), 4324–4330. <u>https://doi.org/10.1021/nn101187z</u>

²⁰ Glasser, L. (1987). Fourier transforms for chemists. Part 1. Introduction to the Fourier transform. *Journal of Chemical Education*, 64(10), A228. <u>https://doi.org/10.1021/ed064pa228</u>

²¹ Mitsuo Tasumi, & Akira Sakamoto. (2015). *Introduction to experimental infrared spectroscopy*. John Wiley & Sons Ltd., , Cop.

²² Berera, R., van Grondelle, R., & Kennis, J. T. M. (2009). Ultrafast transient absorption spectroscopy: principles and application to photosynthetic systems. *Photosynthesis Research*, *101*(2-3), 105–118. https://doi.org/10.1007/s11120-009-9454-y

²³ Einstein, A. (1905). Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. *Annalen Der Physik*, *322*(6), 132–148. <u>https://doi.org/10.1002/andp.19053220607</u>

²⁴ SIEGBAHN, K. (1981, December 8). *ELECTRON SPECTROSCOPY FOR ATOMS, MOLECULES AND CONDENSED MATTER* [Institute of Physics, University of Uppsala, Sweden *ELECTRON SPECTROSCOPY FOR ATOMS, MOLECULES AND CONDENSED MATTER*]. <u>https://www.nobelprize.org/uploads/2018/06/siegbahn-lecture-1.pdf</u>]

²⁵ Hercules, D. M. (2004). Electron Spectroscopy: Applications for Chemical Analysis. *Journal of Chemical Education*. <u>https://doi.org/10.1021/ed081p1751</u>

²⁶ Challa S S R Kumar, & Springerlink (Online Service. (2015). *Surface Science Tools for Nanomaterials Characterization*. Springer Berlin Heidelberg.

²⁷ De Broglie, L. (1925). Recherches sur la théorie des Quanta. *Annales de Physique*, 10(3), 22–128. https://doi.org/10.1051/anphys/192510030022

²⁸ Schatten, H. (2012). *Scanning Electron Microscopy for the Life Sciences*. Cambridge Cambridge University Press.

²⁹ Davisson, C., & Germer, L. H. (1927). Diffraction of Electrons by a Crystal of Nickel. *Physical Review*, *30*(6), 705–740. <u>https://doi.org/10.1103/physrev.30.705</u>

³⁰ Gelderblom, H. R., & Krüger, D. H. (2014). Helmut Ruska (1908–1973). *Advances in Imaging and Electron Physics*, 1–94. <u>https://doi.org/10.1016/b978-0-12-800146-2.00001-1</u>

³¹ C Barry Carter, & Williams, D. B. (2016). *Transmission Electron Microscopy Diffraction, Imaging, and Spectrometry*. Cham Springer International Publishing.

³² Kirstein, S. (1999). Scanning near-field optical microscopy. *Current Opinion in Colloid & Interface Science*, 4(4), 256–264. <u>https://doi.org/10.1016/s1359-0294(99)90005-5</u>

³³ Near-Field Optical Imaging and Spectroscopy Centre. (2024, May 24). The University of Sheffield. https://www.sheffield.ac.uk/nearfield-optical-spectroscopy

³⁴ 3D Optical Profiler - Equipment and Facilities. (n.d.). Henry Royce Institute. <u>https://www.royce.ac.uk/equipment-and-facilities/3d-optical-profiler/</u> 3. Computational chemistry, Quantum Mechanics, and Theoretical Methods.

CONTENTS

Abbreviation	15	78
3.3. Quan	tum Mechanics	80
3.3.1.	History of Quantum Mechanics	80
3.3.1.1.	Heisenberg Uncertainty Principle	81
3.3.1.2.	The Wavefunction	81
3.3.2.	Terminology of Quantum Mechanics: Operators and Eigenvalues	82
3.3.2.1.	Operators	82
Eigen	functions and Eigenvalues	82
3.3.3.	Schrödinger's Equation	82
3.3.3.1.	Time Independent Schrödinger's Equation	82
3.3.3.2.	Time Dependent Schrödinger's Equation	83
3.3.3.3.	The Three-Dimensional, Many-Particle Schrödinger Equation	83
3.3.4.	Born-Oppenheimer Approximation Method for Polyatomic Molecules	84
3.3.5.	Hartree-Fock Theory	85
3.3.5.1.	The Slater Determinant	85
3.3.5.2.	Hartree-Fock Method	86
3.3.5.3.	Limitations of the Hartree-Fock theory	87
3.3.6.	Basis Sets	87
3.3.6.1.	The Linear Combination of Atomic Orbitals	88
3.4. Dens	ity Functional Theory (DFT)	89
3.4.1.	Hohenberg-Kohn Theorem	89
3.4.1.1.	The First Hohenberg-Kohn Theorem	89
3.4.1.2.	The Second Hohenberg-Kohn Theorem	89
3.4.2.	Kohn-Sham Theory	89
3.4.2.1.	Kohn-Sham Orbitals	90
3.4.3.	DFT Functionals	90
3.4.3.1.	The Exchange-Correlation Functional	91
3.4.3.2.	Classes of DFT Functionals	91
3.4.3.3.	Local Density Approximation	92
3.4.3.4.	Generalised Gradient Approximation (GGA)	92
3.4.3.5.	Non-Local Functionals	93
3.5. Bloch	's Theorem	94
3.4. Comp	putational Methods	95
3.4.1.	SIESTA	95
3.4.1.1.	Optical Properties	95

3.4.1.2.	Density of States (DOS)	95
3.4.1.3.	Band Structures	95
3.4.2.	Gaussian	96
3.5. Othe	r Software Used	97
3.5.1.	VESTA	97
3.5.2.	Avogadro	97
3.5.3.	Nanotube Modeler	97
3.6. Refer	rences	

ABBREVIATIONS

Acronym Description

- **DFT** Density Functional Theory
- **DOS** Density of States
- **GGA** Generalised Gradient Approximation
- **GTO** Gaussian-type orbitals
- LDA Local Density Approximation
- **SIESTA** Spanish Initiative for Electronic Simulations with Thousands of Atoms
- **STO** Slater-type orbitals
- **TDSE** Time-Dependent Schrödinger Equation
- **TISE** Time-Independent Schrödinger Equation

Computational chemistry, Quantum Mechanics, and Theoretical Methods.

Computational modelling has become an indispensable tool in modern chemical research, driving advancements across various fields, particularly for understanding the properties of novel materials like graphene. It is extensively used to predict and explain a vast array of phenomena at the molecular and material level. These applications include, but are not limited to, predicting features in electronic absorption spectra, calculating band structures, and comprehending the mechanisms of reactions. Performing these simulations often requires specialised software and significant computational power. This is especially true for theoretical chemists who leverage the principles of quantum mechanics to predict how molecules and materials will behave in experiments, based on the interactions between atomic nuclei and electrons.¹

3.3. QUANTUM MECHANICS

"For those who are not shaken when they first come across quantum theory cannot possibly have understood it" -Neil Bohr $^{\rm 2}$

3.3.1. History of Quantum Mechanics

Thomas Young, in 1803, gave convincing evidence for the wave nature of light: he demonstrated diffraction and interference of light, confirming its wave-like behaviour.^{3,4} In 1864, James Clerk Maxwell unified electricity and magnetism, therefore predicting light as an electromagnetic wave travelling at a constant speed (*c*), described by the Maxwell equations.⁵ In 1888, Heinrich Hertz detected radio waves produced by accelerated electric charges in a spark,⁶ as predicted by Maxwell's equations. This convinced physicists that light is indeed an electromagnetic wave.⁷

In the 1890s, measurements of light emitted by heated objects, known as blackbody radiation, did not match predictions from classical physics, particularly at low frequencies. In the 1900s Planck started the quantum mechanics 'revolution', when he discovered the equation for the distribution of radiation emitted by a blackbody.⁷ Max Planck proposed that energy emitted by blackbodies comes in discrete packets called quanta, each with energy proportional to frequency as described in section 2.1.2.⁸

"Briefly summarised, what I did can be simply an act of desperation"-Max Planck ⁹

In 1905 Albert Einstein explained the photoelectric effect using light quanta (photons).¹⁰ He showed that the energy of ejected electrons depended on the light's frequency, not its intensity, contradicting classical wave theory.¹¹

$$\lambda v = c \tag{3.1}$$

$$E_{photon} = hv \tag{3.2}$$

Ernest Rutherford's experiments in 1911 revealed the nucleus-electron model of the atom, with a tiny, dense nucleus containing most of the mass and electrons orbiting around it, and in 1913 Niels Bohr applied quantisation to electron energy levels in the hydrogen atom, explaining its discrete spectral lines. He proposed that electrons occupied specific allowed orbits, and transitions between them emitted or absorbed photons with energies matching the difference in the orbits' energies.^{12,13}

$$E_{upper} - E_{lower} = hv \tag{3.3}$$

Prince Louis de Broglie in 1923 proposed that electrons, like photons, could exhibit wave-like behaviour with a wavelength related to their momentum (represented in Equation (3.4)), and in 1927 Clinton Davisson and Lester Germer verified de Broglie's hypothesis by observing electron diffraction, demonstrating the wave-particle duality of matter.^{14,15}

$$\lambda = \frac{h}{p} \tag{3.4}$$

 λ = the de Broglie wavelength (m), h = Planck's constant¹⁶ (6.63 × 10⁻³⁴ J s), p = momentum of a particle (kg m/s) (p = mv)

In 1926, Erwin Schrödinger developed a wave equation (Schrödinger equation) to describe the wave function of a quantum particle, providing a more complete framework for understanding quantum mechanics.^{7,8,17}

After these foundational studies, it was established that energy and other physical properties can only exist in discrete values, not continuously. Matter and light can exhibit wave-like or particle-like behaviour depending on the experimental setup.

3.3.1.1. Heisenberg Uncertainty Principle

As previously discussed, electromagnetic fields and oscillating electrons have quantised energies. The particle character of electromagnetic radiation explains that light can possess discrete energies (hv, 2hv, ...) meaning that light comes in packets called photons, each with energy hv.

The photoelectric effect demonstrates that when the light above a threshold frequency is directed at a metal, it causes electrons to be ejected with kinetic energy *KE* proportional to the frequency v (*KE* = $hv - \Phi$). This implies that light interacts with electrons as particles (photons).

Experiments aimed at studying electrons led to the discovery of a connection between a particle's momentum and its associated wavelength. This relationship, expressed as in equation (3.4), explains why larger objects with high momentum don't exhibit this wave-like behaviour. Their wavelengths are incredibly small, making their wave nature undetectable in our everyday world. Wave-particle duality refers to the idea that light and matter exhibit both particle and wave characteristics, defying classical categorisation, and that both light and matter exhibit discrete energy levels, contradicting the continuous properties in classical mechanics. Equation (3.2) expresses the quantisation of energy.

The Heisenberg uncertainty principle is a fundamental concept in quantum mechanics that states that a quantum particle's position and momentum cannot be known with perfect accuracy simultaneously. Prior to measurement, the particle can exist in a superposition of multiple states. However, the act of measurement collapses this superposition, forcing the particle into a single definite state. It is explained mathematically through the commutation relation between operators representing conjugate pairs of properties.¹¹

 $[x, p] = i\hbar$ (3.5) Where *i* is the imaginary unit, \hbar = reduced Planck constant = $h/2\pi$, x = position and p is the momentum.

The minimum achievable product of the uncertainties in simultaneously measuring two uncertainties is governed by a fundamental limit, meaning that for position and momentum measurements, the uncertainty principle dictates that their product cannot be smaller than $\hbar/2$. This uncertainty relation states that attempting to measure one property more precisely essentially increases the uncertainty of the other. This constraint originates from the wave-particle duality of matter. A narrower packet (smaller Δx) implies a more localised position but also requires a wider spread of frequencies (larger Δp) within the packet. On the other hand, a wider packet (larger Δx) has a narrower frequency range (smaller Δp). This link between the spread in position and momentum reflects the wave-particle duality.¹¹

$$\Delta x \, \times \, \Delta p \, \ge \, \frac{\hbar}{2} \tag{3.6}$$

This can also be written as:

$$\Delta x \, \times \, \Delta p \, \ge \frac{h}{4\pi} \tag{3.7}$$

Where Δx is the uncertainty in position and Δp is the uncertainty in momentum.

3.3.1.2. The Wavefunction

In the realm of quantum mechanics, the wave function is a mathematical expression that captures the wave-like characteristics of a system or particle. It serves as a comprehensive representation of all the information available about the physical state of said system or particle. To effectively describe a system's state in quantum mechanics, a function denoted as Ψ must be utilised. This function, also known as the state function or wavefunction, encapsulates the coordinates of the particles in question.

3.3.2. Terminology of Quantum Mechanics: Operators and Eigenvalues

3.3.2.1. Operators

An operator (\hat{O}) is a set of instructions for creating a function from another function, while a superoperator is a set of instructions for creating an operator from another operator. The concept of operator algebra is similar to matrix algebra, since matrices can be viewed as representations of operators within a particular set of functions or coordinate system. It is worth noting that most operators used in computational chemistry are linear and that operators are associative but not necessarily commutative. An operator qualifies as linear if it follows the two principles of homogeneity (also known as scaling) and additivity. Homogeneity involves scaling both the wave function and the output by the same constant, while additivity means that applying the operator to a sum of wavefunctions yields the same result as applying it to each wavefunction individually and then summing the results. Associativity, in terms of operators, states that the order of grouping operators does not influence the final outcome. However, some operators, such as momentum and position, are non-commutative, which means that the order to apply them can significantly impact the outcome.¹⁸

Eigenfunctions and Eigenvalues

Eigen is a German word meaning "characteristic". Eigenfunctions and eigenvalues play a critical role in various fields of quantum mechanics and signal processing. An eigenvalue is a specific value linked to a linear transformation (operator). If applied to an eigenvector, the operator scales the eigenvector by the eigenvalue while keeping the direction constant.¹⁸

3.3.3. Schrödinger's Equation

De Broglie's wave-particle duality inspired Schrödinger to develop a wave-based explanation of quantum systems. He recognised that classical waves follow wave equations and, therefore, sought to derive an equation for the "quantum wave" associated with a particle. He translated classical concepts such as momentum and energy into quantum operators using matrices and integrated them into a wave equation. Building on insights from Hamilton's mechanics and de Broglie's research, Schrödinger ultimately formulated the notable Schrödinger equation in 1926.⁸

3.3.3.1. Time Independent Schrödinger's Equation

The time-independent Schrödinger's equation (Equation (3.8)) is applicable when the system's energy is independent of time.

$$\widehat{H}\Psi = E\Psi \tag{3.8}$$

Where Ψ = wavefunction, \hat{H} = Hamiltonian operator and E = energy

While the Schrödinger equation allows us to calculate the wavefunction, it doesn't directly reveal its physical significance. Max Born theorised that the wavefunction represents a probability amplitude and that the squared magnitude of the wavefunction describes the probability of an electron existing in a specific location. Solving the time-independent Schrödinger equation yields the wave function or state function of a quantum-mechanical system, which governs the motion of nuclei and electrons through their wavefunction. This equation is crucial for determining the allowed energy levels in quantum mechanical systems.¹⁹ In this case, the wave function ($\Psi(x)$) only depends on the position (x). Solving the time independent Schrödinger's equation (TISE) provides the energy eigenstates of the system, which are stationary states with constant energy. The general form of the TI-SE, denoted as Equation (3.8), governs the behaviour of quantum systems with constant total energy. This equation applies to systems with any number of particles and spatial dimensions. Equation (3.9) represents a specific case of the TISE, tailored for systems with only one particle confined to a one-dimensional space.

$$-\frac{\hbar^2}{2m} \frac{d^2 \Psi(x)}{dx^2} + V(x)\Psi(x) = E\Psi(x)$$
(3.9)

Where V(x) represents the potential energy of the system in the Schrödinger Equation, which depends on the position (x), and m is the mass of the particle.

Solving the time-independent Schrödinger's equation allows the determination of ground state energy *E* of the system or molecule.

3.3.3.2. Time Dependent Schrödinger's Equation

Time-dependent Schrödinger's equation (TDSE) is the most general form of the equation and describes how a quantum system evolves over time. The wave function depends on both position and time ($\Psi(x, t)$). The Schrödinger's equation with time-dependence is a crucial formula in quantum mechanics that describes a wide range of problems. These problems encompass the computation of energy levels of atoms and molecules, modelling the movement of electrons, analysing the dynamics of chemical reactions, and comprehending phenomena such as quantum tunnelling.

$$\widehat{H}\Psi = i\hbar \frac{\partial\Psi}{\partial t}$$
(3.10)

The time dependent equation for the one-particle, one-dimensional scenario can also be stated as:

$$\frac{\hbar}{i}\frac{\partial\Psi(x,t)}{\partial t} = -\frac{\hbar^2}{2m}\frac{\partial^2\Psi(x,t)}{\partial x^2} + V(x,t)\Psi(x,t)$$
(3.11)

3.3.3.3. The Three-Dimensional, Many-Particle Schrödinger Equation

Both TDSE and TISE can be used to describe systems with multiple particles. In three dimensions, the equations involve the positions of all particles simultaneously. Equations (3.8) and (3.10) both use a single wave function, Ψ , to describe all particles in the system simultaneously. The wave function depends on the spatial coordinates ($x_1, x_2, ..., x_n$) of all particles in the three-dimensional space.

 $\Psi(x_1, x_2, ..., x_n, t)$ in the TDSE represents the wave function as a function of the positions and times of all particles, while in the TISE $\Psi(x_1, x_2, ..., x_n)$ represents the wave function as a function of only the positions of all particles.

Classically, the total energy of a system can be written as equation (3.25).

$$E = T + V \tag{3.12}$$

Where E = energy, T = kinetic energy and V = potential energy

As mentioned before, the Hamiltonian can be used to find the total energy of a system. According to the equation above, the Hamiltonian operator can be separated into two parts or two operators that correspond to the potential and kinetic energies.

$$\widehat{H} = \widehat{T} + \widehat{V} \tag{3.13}$$

Where \hat{H} is the Hamiltonian, \hat{T} is the kinetic energy operator and \hat{V} is the potential energy operator.

The kinetic energy operator for a particle is:

$$\hat{T} = -\frac{\hbar^2}{2m} \nabla^2$$
(3.14)

e), $\nabla^2 = \frac{d^2}{dx^2} + \frac{d^2}{dy^2} + \frac{d^2}{dz^2}$

 ∇^2 = the Laplacian (second derivative),

 \hat{V} can be written using Coulomb's law, it is a multiplicative operator. For interactions between two electrons, it has the form:

$$\hat{V}(x) = + \frac{e^2}{4\pi\varepsilon_0} \frac{1}{r}$$
(3.15)

The kinetic energy of electrons *i* is written as:

The kinetic energy of nuclei A is stated as:

$$-\frac{\hbar^2}{2m_e}\sum_{i}^{\infty}\nabla_i^2$$
$$-\frac{\hbar^2}{2}\sum_{i}\frac{1}{M_A}\nabla_A^2$$

n

The potential energy includes the following energies:

The nuclei-nuclei interactions:

The nuclei- electrons interactions:

The electrons- electrons interactions:

The overall potential energy is

$$\frac{e^2}{4\pi\varepsilon_0} \sum_{A>B} \frac{Z_A Z_B}{R_{AB}}$$

$$\frac{e^2}{4\pi\varepsilon_0} \left(-\sum_{A} \frac{Z_A}{r_{A,i}}\right)$$

$$\frac{e^2}{4\pi\varepsilon_0} \sum_{I>I} \frac{1}{r_{IJ}}$$

$$\frac{e^2}{4\pi\varepsilon_0} \left(\sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{A,I} \frac{Z_A}{r_{A,I}} + \sum_{I>I}\right)$$

Consequently, the Hamiltonian operator for a n-particle, three-dimensional system of electrons and nuclei is:

$$\widehat{H} = -\frac{\hbar^2}{2m_e} \sum_{i} \nabla_{i}^{2} - \frac{\hbar^2}{2} \sum_{A} \frac{1}{M_A} \nabla_{A}^{2} + \frac{e^2}{4\pi\epsilon_0} \left(\sum_{A>B} \frac{Z_A Z_B}{R_{AB}} - \sum_{Ai} \frac{Z_A}{r_{A,i}} + \sum_{i>i} \frac{1}{r_{ij}} \right)$$
(3.16)

Where, ∇^2_i = Laplacian operator for electrons, ∇^2_A = Laplacian operator for the nuclei, ε_0 = permittivity of free space, m_e = mass of an electron, M_A = mass of the nucleus, R_{AB} = nuclear-nuclear distance, $r_{A,i}$ = nuclear-electron distance, $r_{i,j}$ = electron-electron distance and $Z_{A,B}$ = nuclear charges.

3.3.4. Born-Oppenheimer Approximation Method for Polyatomic Molecules

Dealing with molecules that possess multiple electrons and nuclei can be a complex process, as the Schrödinger equation involves many variables. Even relatively small molecules present a computational impossibility when solving the equation exactly. To surmount this obstacle, the Born-Oppenheimer approximation is introduced. Max Born and J. Robert Oppenheimer proposed in 1927 that the motion of electrons and nuclei can be approximated to be separable due to the mass and speed of electrons and nuclei being different. By leveraging the disparity in mass between electrons and nuclei, the approximation assumes that electronic motion occurs significantly faster than nuclear motion. This division of electronic and nuclear movements simplifies the problem at hand.²⁰ The molecular wavefunction $\Psi_{molecule}$ is a function of electron positions r_i and nuclear positions R_i .

$$\Psi_{molecule}(r_i, R_j) = \psi_{electron}(r_i, R_j)\psi_{nuclei}(R_j)$$
(3.17)

The nuclei, being much heavier than electrons, move much more slowly. They can be treated as point charges with very narrow wave packets. In the Born-Oppenheimer approximation, the Schrödinger equation is solved for the electrons while the nuclei are assumed to be stationary. The fixed positions of the nuclei determine the distribution of the electrons due to the electrostatic forces exerted by the nuclei. While it is true that electrostatic forces from the electrons influence the nuclei, in this approximation, the nuclei are considered fixed, and their positions dictate the arrangement of the electrons rather than the reverse. This approximation allows for the separation of the motions of the electrons and nuclei, with the electrons moving quickly within the field and the nuclei assumed to be stationary. This decoupling of the motions of electrons and nuclei simplifies the Hamiltonian operator only to consider the movement of electrons. The Born-Oppenheimer approximation considers the

nuclei to move on a potential energy surface, which is a solution to the electronic Schrödinger equation.¹⁸

$$\widehat{H}_{el} = \widehat{T}_e + \widehat{V}_{ee} + \widehat{V}_{nn} + \widehat{V}_{ne}$$
(3.18)

Where \hat{H}_{el} = the electronic Hamiltonian, \hat{V}_{ne} = attractive potential energy between the nuclei and electron, \hat{V}_{ee} = the repulsive potential energy for the electron-electron interactions and \hat{T}_{e} = kinetic energy of electrons. In this approximation \hat{V}_{nn} is constant.

$$\widehat{H}_{el}\,\psi_{el} = E_{el}\,\psi_{el} \tag{3.19}$$

Where $\widehat{\Psi}_{el}$ = the electronic wave function and E_{el} = electronic energy.

The Born- Oppenheimer (BO) approximation is widely applied and forms the basis of many quantumchemical methods; however, it has some limitations, i.e. it is applicable only to non-adiabatic processes.

In the Born-Oppenheimer approximation, an adiabatic process occurs when the nuclei in a molecule move slowly enough compared to the changes in the electronic structure. The adiabatic approximation supposes that the lighter electrons adjust adiabatically to the motion of the heavier nuclei, remaining at any time in their instantaneous ground state.²¹ This allows the electronic motion to be treated as nearly instantaneous, following the nuclei as they move. As a result, the electrons are assumed to be in their ground electronic state for any given nuclear configuration. This simplification significantly reduces the complexity of calculations.

On the other hand, a nonadiabatic process occurs when the nuclei move too rapidly relative to the electronic response. In such cases, the electrons cannot adjust instantaneously to the changing nuclear positions, making them excited to higher electronic states. This coupling between the nuclear and electronic motion results in additional effects not captured by the Born-Oppenheimer approximation.¹⁸

The BO approximation is valid only when the changes in the system occur slowly enough to be considered adiabatic. If the system undergoes fast changes or strong interactions between electronic states, nonadiabatic effects become significant, and the Born-Oppenheimer approximation breaks down, for example, in certain excited states of polyatomic molecules and for certain ground states of cations. In such cases, more advanced methods that account for these interactions are required to accurately describe the system's behaviour.

3.3.5. Hartree-Fock Theory

The Hartree-Fock method is a quantum mechanical approach that utilises the Born Oppenheimer approximation and assumes that the electronic wave function can be expressed as a single Slater determinant, which enforces an antisymmetric wave function complying with the Pauli exclusion principle. The exclusion principle states that no two electrons in the same atom or molecule can have identical quantum number values. In this context, antisymmetry refers to the requirement that the wave function changes sign when any two electrons are interchanged. This condition ensures that the likelihood of locating two electrons with matching quantum states in the same position is zero, as dictated by the Pauli exclusion principle. Antisymmetry is a fundamental aspect of fermion behaviour, particularly for electrons, and it forms the basis for the structure and characteristics of atoms and molecules.^{22,23}

3.3.5.1. The Slater Determinant

To fulfil the antisymmetry requirement, the HF method constructs the wave function using Slater determinants, where χ represents a spin-orbital^{24,25}

$$\psi = \frac{1}{\sqrt{N!}} \begin{vmatrix} \chi_{1}(x_{1}) & \chi_{2}(x_{1}) \cdots & \chi_{N}(x_{1}) \\ \chi_{1}(x_{2}) & \chi_{2}(x_{1}) & \chi_{N}(x_{2}) \\ \vdots & \vdots & \ddots & \vdots \\ \chi_{1}(x_{N}) & \chi_{2}(x_{N}) & \chi_{N}(x_{N}) \end{vmatrix}$$

Slater determinant can be written in the shorthand notation as follows:

$$\psi = |\chi_i \chi_i \dots \chi_N\rangle \text{ or } |ij \dots N\rangle$$
(3.20)

3.3.5.2. Hartree-Fock Method

The Hartree-Fock molecular orbital theory aims to solve the electronic Schrödinger equation approximately while neglecting the relativistic effects, assuming electron velocities are significantly lower than the speed of light which is often valid for most chemical systems.¹⁸ Equation (3.21) provides a more detailed representation of the electronic Hamiltonian compared to equation (3.19) by including the coordinates of the electrons and nuclei.

$$\widehat{H}_{el}(r;R)\psi(r;R) = E_{el}(R)\psi(r;R)$$
(3.21)

Where r = coordinates of electrons and R = coordinates of the nuclei, which in this approximation are frozen in space.

According to the Hartree-Fock's theory, each electron interacts only with the average charge cloud of other electrons.¹⁸ The Hamiltonian can be represented as a sum of one-electron and two-electron operators. The one-electron operator incorporates both the kinetic energy of the electron and its potential energy of interaction with all the nuclei in the molecule. The one-electron operator for electron *i* is:

$$\hat{h}(i) = -\frac{1}{2}\nabla_i^2 - \sum_A \frac{Z_A}{r_{ij}}$$
(3.22)

Where Z_A = the charge on the nucleus, r_{ij} = the distance between electron and nucleus and A = the nucleus. \hat{h} includes the kinetic energy of an electron and its potential energy of attraction to all the nuclei.

The two-electron operator for electrons *i* and *j* describes their Coulomb repulsion:

$$\hat{v}(ij) = \frac{1}{r_{ii}} \tag{3.23}$$

As the nuclei are considered to be motionless, the electronic Hamiltonian is expressed as:

$$\hat{H}_{el} = \sum_{i} \hat{h}(i) + \sum_{i < j} \hat{v}(i, j) + V_{NN}$$
(3.24)

Where, $\sum_i \hat{h}(i)$ = the sum of one-electron operators, $\sum_{i < j} \hat{v}(i, j)$ = the sum of repulsion of all unique pairs of electrons and V_{NN} = constant nuclear-nuclear repulsion term.

Following from this separation of the Hamiltonian into the one-electron and two-electron terms, the electronic energy *E* in the Hartree-Fock approximation can be represented as:

$$E_{HF} = \sum_{i}^{elec} \langle i|\hat{h}|i\rangle + \sum_{i>j}^{elec} [ii|jj] - [ij|ji]$$
(3.25)

Where $\sum_{i}^{elec} \langle i | \hat{h} | i \rangle$ is the one-electron term representing electron-nuclear attraction and electron kinetic energy, $\sum_{i>j}^{elec} [ii|jj] - [ij|ji]$ is the two-electron term, representing electron-electron repulsion and the anti-symmetry of electrons. In the two-electron term, [ii|jj] is the Coulomb integral which describes repulsion for each pair of electrons in *i* and *j*, and [ij|ji] is the exchange integral which describes the antisymmetry required by the Pauli principle.

This gives a Hartee-Fock expression for the energy of:

$$E_{HF} = \sum_{i=1}^{n} H_i + \frac{1}{2} \sum_{i=1}^{n} \sum_{j=1}^{n} (J_{i,j} - K_{i,j})$$
(3.26)

Where H_i = one electron Hamiltonian which represents the electron-nuclear attraction and kinetic energy of an electron in a spin-orbital; the Coulomb term, $J_{i,j}$, represents the electrostatic repulsion between two electrons *i* and *j*; $K_{i,j}$ is the exchange term, which accounts for the Pauli Antisymmetry principle. J_{ij} and K_{ij} are two-electron matrix element terms dependent on the wavefunction.

The key approximation in HF theory assumes that each electron moves independently in an average potential energy field created by the other electrons. The self-consistent field (SCF) method is used in Hartree-Fock theory to solve a set of coupled equations for the *n* electrons, iteratively updating the MOs and the Hamiltonian until self-consistency is achieved to determine molecular orbitals which minimise the electronic energy.¹⁸

The Restricted Hartree-Fock (RHF) method is most suitable for closed-shell molecules, which have equal numbers of electrons with opposite spins. It requires that the two electrons in each spatial orbital have opposite spins, resulting in each MO being doubly occupied by an α and a β electron. RHF calculations are generally faster and less complex than Unrestricted Hartree-Fock (UHF) calculations due to this spin restriction. However, they are not suitable for open-shell molecules, which have unpaired electrons that make the spin constraint unrealistic.¹

On the other hand, the UHF method is designed for open-shell molecules with unpaired electrons. It allows for different spatial orbitals for α and β electrons, providing more flexibility in describing the electronic structure of such systems. However, UHF calculations involve solving a larger set of equations due to the relaxed spin constraint, leading to increased computational cost. Although UHF offers more flexibility, it may sometimes suffer from spin contamination. This happens when the wave function is not purely a single determinant and includes contributions from excited states, resulting in inaccuracies in certain properties.¹

3.3.5.3. Limitations of the Hartree-Fock theory

While the Hartree-Fock method has been successful in many areas, it does have some limitations and lacks computational efficiency. For instance, it doesn't account for the instantaneous repulsion between individual electrons, which leads to an underestimation of the electronic energy compared to the true value. The mean-field approach averages the electron interactions and therefore ignores dynamic electron correlation: it assumes that each electron moves in an average field created by the other electrons, but this average field is not entirely accurate due to the fluctuating positions of other electrons caused by their quantum nature.

Furthermore, the Hartree-Fock method struggles with open-shell systems since the single determinant used cannot fully capture the complex interactions between unpaired electrons. It's also worth noting that Hartree-Fock calculations cannot account for dispersion forces that arise from instantaneous fluctuations in electron density.¹⁸

In this research, the Hartree–Fock method was implemented using Gaussian software for the calculations that are later mentioned in Chapter 9. Its primary significance lies in introducing fundamental concepts that form the foundation for more advanced methods, such as Density Functional Theory.

3.3.6. Basis Sets

When carrying out Hartree-Fock or other quantum chemical calculations, basis functions are used, referred to as basis sets. A basis set is a collection of mathematical functions used to approximate the electronic wave function, which describes the behaviour of electrons in a molecule.¹⁸ A molecular

orbital can be described by an infinite number of basis functions in a complete basis set. However, when using a finite basis set, only a portion of the molecular orbital can be represented. As a result, smaller basis sets can result in faster calculations but less accuracy. To choose the most appropriate basis set, two conflicting requirements need to be considered. Firstly, the basis set must contain as many different functions as possible so that the molecular orbitals created from the combination of the different basis functions closely resemble the true molecular orbitals. Secondly, the basis sets should be kept as small as possible to ensure computational efficiency for a given level of accuracy.¹

3.3.6.1. The Linear Combination of Atomic Orbitals

Since an infinite number of functions in a complete basis set is impractical, finite basis sets are employed, resulting in approximate molecular wavefunctions. The Linear Combination of Atomic Orbitals (LCAO) basis sets method combines multiple atomic orbitals from individual atoms in a molecule. These orbitals are localised around atoms and are represented as products of a radial function and a spherical harmonic. Additional basis functions with increasing values of the quantum numbers can be used, allowing for systematic improvement of accuracy. The SIESTA calculations done in this work involve the use of numerically localised atomic orbitals.

The two common types of basis functions are Slater-type orbitals (STOs) and Gaussian-type orbitals (GTOs), with combinations of GTOs being more computationally efficient and commonly used in modern calculations.^{18,23} GTOs are mathematical functions that approximate the behaviour of electrons in atoms and molecules in a simplified form. Unlike Slater-type orbitals, which are more accurate but have a more complex mathematical form, GTOs have a smooth bell-curve shape and a simple exponential form that makes them easier to use in computations. This computational efficiency makes GTOs the preferred choice in most electronic structure calculations, where they are combined to represent the complex shapes of real electron orbitals. Although single GTOs do not perfectly model electron behaviour near the nucleus and in the outer regions, use of combinations of GTOs improved on their accuracy, so that their computational advantages outweigh this slight loss of accuracy for most applications.¹⁸ The Gaussian calculations mentioned in Chapter 9 in this work used Gaussian-type orbitals.

3.4. DENSITY FUNCTIONAL THEORY (DFT)

Density functional theory (DFT) has become a very popular method in chemistry, physics, and materials science for studying the behaviour of systems with many electrons. It offers significant advantages, particularly in terms of reduced computational cost compared to traditional wavefunction-based methods. However, the accuracy of agreement with experimental data depends on the specific method used in both DFT and wavefunction approaches. Unlike wavefunction-based methods, DFT relies on the electron density (ρ), which is a function that represents the probability of finding an electron at a particular location. The success of modern DFT methods is based on the suggestion by Kohn and Sham in 1965 that the electron density.¹⁸ Density Functional Theory is a well-established method, and its computational efficiency compared to wavefunction-based methods makes it a popular choice for large-scale calculations involving complex systems with many electrons.

3.4.1. Hohenberg-Kohn Theorem

The Hohenberg-Kohn (HK) Theorems are a set of fundamental principles that serve as the foundation of modern Density Functional Theory. These theorems establish a fundamental connection between the electron density ($\rho(r)$) of a system and its ground-state properties, which is critical for understanding the behaviour of complex systems and predicting their properties.^{18,26}

3.4.1.1. The First Hohenberg-Kohn Theorem

The initial hypothesis of the HK theory posits a distinct correlation between the electron density $(\rho(r))$ and the fundamental characteristics of a system's ground state. It establishes that different external potentials cannot produce identical ground-state densities, thereby indicating that the density is unequivocally related to the external potential and, by extension, the Hamiltonian and ground-state properties of the entire system. This theorem serves as the cornerstone of DFT by demonstrating that the electron density, which is computationally less complex than the wave function, can encapsulate all the pertinent information about a system.¹⁸

3.4.1.2. The Second Hohenberg-Kohn Theorem

The second Hohenberg-Kohn theorem introduces a variational principle as applied to DFT. According to this principle, the functional that determines the ground-state energy $(E[\rho])$ only attains its minimum value when the input density (ρ (r)) corresponds to the true ground-state density (ρ 0). This principle is useful for evaluating the accuracy of a trial density by comparing its energy with the true ground-state energy. However, it is important to note that the second theorem has its limitations, as it applies strictly to the ground state and not directly to excited states.¹⁸

3.4.2. Kohn-Sham Theory

The main challenge in DFT is to accurately determine the electron kinetic and potential energy terms as a function of electron density, which involves dealing with complex interactions among electrons. The Kohn-Sham (KS) equations provide a solution by introducing a system of non-interacting electrons and formulating a set of single-electron equations. These equations are much simpler to solve computationally compared to the full many-electron problem. The solutions, referred to as the Kohn-Sham orbitals, are then used to calculate the electron density.

In this approach, the total energy E[p] determined in DFT calculations can be divided into several components as follows:

$$E[\rho] = T_{ni}[\rho] + V_{ne}[\rho] + V_{ee}[\rho] + \Delta T + \Delta V_{ee}[\rho]$$
(3.27)

Where ρ = ground state electron density for a system, Tni = kinetic energy of non-interacting electrons, Vne = nuclear-electron interaction, Vee = classical electron-electron repulsion, ΔT = correction to the kinetic energy for an interacting system, ΔVee = non-classical correction to the potential energy of electron-electron interaction, $E_{xc} = \Delta T + \Delta Vee$ and Exc= exchange-correlation functional.

The exchange-correlation functional Exc, is key in Kohn-Sham DFT, as it captures the complex manybody effects of electron exchange and correlation that are otherwise difficult to model directly.

This approach effectively bridges the gap between a simplified non-interacting system and the real interacting system by introducing corrections that account for the complexities of electron interactions while still allowing for computational efficiency.

The effective potential is defined as a combination of the classical electrostatic potentials produced by the nuclei and the electrons, followed by adding the exchange-correlation potential.

$$V_{eff} = \{V_{ne}(r) + V_{ee}[\rho(r)] + V_{XC}[\rho(r)]\}$$
(3.28)

After calculating the effective potential, the Schrödinger equation is solved by expanding the wave function in a basis set. This reduces the Schrödinger equation to a matrix eigenvalue problem:

$$\begin{bmatrix} -\left(\frac{1}{2}\right)\nabla^2 + V_{eff}(r) \end{bmatrix} \psi_i(r) = E_i \psi_i(r)$$

$$\psi_i(r) = \Sigma_{\mu} C_{i\mu} \Phi_{\mu}(r)$$

$$\downarrow$$

$$\Sigma_{\nu} H_{\mu\nu} C_{i\nu} = E_i C_{i\mu}$$

A new density is found as the square of the electron wavefunctions.

$$\rho(r) = \Sigma_i |\psi_i(r)|^2 \tag{3.29}$$

This self-consistent cycle of calculation is repeated until the density no longer changes.

3.4.2.1. Kohn-Sham Orbitals

As mentioned above, Kohn-Sham orbitals are a theoretical construct utilised in DFT calculations to simplify the complex issue of electron interaction in molecules. They do not directly represent real physical orbitals, but instead serve as a tool to compute electron density, a crucial factor in DFT. While they are not physically real, they bear a resemblance to Hartree-Fock molecular orbitals and can be used to qualitatively understand molecular properties and reactivity.⁷

Generally, KS orbital energies do not match the energy needed to extract an electron from a molecule, unlike Hartree-Fock orbitals. The one exception is the highest occupied Kohn-Sham orbital, which can be linked to the first ionisation energy. Therefore, the current approximations used in DFT calculations frequently result in imprecise predictions of molecular properties related to orbital energies, particularly ionisation energies.

Ideally, DFT equations would be solved directly with the electron density without involving orbitals. However, since the precise functional relationship between energy and density is unknown, the Kohn-Sham method is utilised as a practical compromise. Various approximate functionals are used in DFT calculations. To evaluate the accuracy of a functional, one can use it in DFT calculations and compare the calculated molecular properties with experimental ones. A major drawback of DFT is that there is no systematic approach to improving the accuracy of these approximations.⁷ As defined in Equation (30), the exchange-correlation functional includes both the non-classical electron-electron interactions and the correction to the kinetic energy of a fictitious non-interacting system.

$$E_{xc} = \Delta T + \Delta V_{ee} \tag{3.30}$$

3.4.3. DFT Functionals

A function is a recipe for producing a scalar from another set of scalars, and a functional is a recipe for producing a scalar from a function. ¹⁸ In DFT, a functional is a mathematical object that maps a function such as the electron density, $\rho(r)$, to a single scalar value. This value represents a specific property of the system, such as its total energy, kinetic energy, or exchange-correlation energy.

3.4.3.1. The Exchange-Correlation Functional

Kohn-Sham theory relies heavily on the exchange correlation (xc) functional to accurately capture the intricacies of interacting electrons. While the theory simplifies the problem by treating electrons as non-interacting, this simplification introduces an error compared to the true interacting system. The exchange-correlation energy (Exc) in DFT accounts for various effects, including static and dynamic correlation, exchange interactions, and kinetic correlation (the interaction correction to the kinetic energy).

In this context, correlation refers to the tendency of electrons to avoid each other due to their mutual repulsion, not just because of the Pauli exclusion principle. This avoidance applies to both electrons with the same spin and those with opposite spins. Dynamic correlation, particularly relevant for DFT, describes how electrons avoid each other in response to their instantaneous positions, while static correlation deals with systems where electrons are partially localised due to strong interactions.⁷

The (xc) functional is specifically designed to account for complex correlation effects, ensuring that the behaviour of the non-interacting electrons in the Kohn-Sham system mirrors that of real interacting electrons. By doing so, it encompasses both the exchange interactions (where same-spin electrons avoid each other due to the Pauli exclusion principle) and the broader correlation effects arising from electron-electron repulsion. This functional plays a crucial role in obtaining accurate results in DFT, addressing the simplifications made in treating electrons as non-interacting while maintaining computational efficiency.

Kinetic correlation considers the difference in kinetic energy between the real system of interacting electrons and a hypothetical system of non-interacting electrons with the same electron density. In the real system, electrons encounter an average field from other electrons, which alters their motion compared to non-interacting particles. This difference contributes to the total energy.⁷

Exchange interaction arises from the Pauli exclusion principle, which states that electrons with the same spin cannot occupy the same quantum state. This principle results in a repulsive force between electrons with the same spin, which is captured by the exchange term in Exc, beyond the Coulomb repulsion caused by electrons carrying the same electrical charge. This exchange interaction influences the way electrons distribute themselves in space. The (xc) functional incorporates this exchange interaction, ensuring that the non-interacting electrons in the Kohn-Sham system experience a similar repulsive force as the real interacting electrons.

Electron exchange and correlation are important concepts in physics and chemistry that ensure physical accuracy by considering the Fermi and Coulomb holes. These holes represent the depletion of probability around an electron caused by the Pauli Exclusion Principle and electrostatic repulsion between electrons, respectively. The Fermi and Coulomb holes must integrate to the required values of -1 and 0 to ensure accuracy.¹⁸

3.4.3.2. Classes of DFT Functionals

There are different levels of approximation for calculating the electronic structure of materials, which are classified based on the hierarchy of accuracy and complexity of various exchange-correlation functionals, also known as the Jacob's ladder metaphor. These classes or orders represent different levels of approximation for the exchange-correlation energy. First-order functionals exclusively rely on the electron density (ρ), they are the simplest and most computationally efficient type. These functionals are based on the local density approximation (LDA), which assumes that the exchange-correlation energy at each point in space depends only on the local electron density at that point. Second-order functionals take a step further by incorporating the both the electron density and its gradient ($\nabla \rho$), with the exchange functional ($X[\rho, \nabla \rho]$) being the most critical example, as it accounts for the exchange interaction between electrons. Generalised Gradient Approximation (GGA) functionals are example of a second-order functional.

3.4.3.3. Local Density Approximation

The LDA within Density Functional Theory offers a simplified approach to approximating the complex interactions between electrons in a system. This method hinges on a fundamental assumption that the electron density at any given point in space can be treated as if it were part of a homogeneous electron gas.¹⁸

This simplification allows the application of pre-calculated values for the exchange-correlation energy of a uniform electron gas, obtained through highly accurate techniques like quantum Monte Carlo simulations. These pre-calculated values are subsequently employed to approximate the exchange-correlation potential and energy within the actual system, even though the real density may exhibit deviations from perfect uniformity.

As described above, the exchange-correlation potential has two principal underlying interactions that give rise to it. First, the exchange effect states that fermions with identical spin cannot occupy the same quantum state, suggesting that, if the positions of two electrons are swapped, the wavefunction describing them must change sign. Secondly, the correlation effect, which arises from the mutual repulsion between electrons. When one electron is present, it affects the distribution of other electrons, which prevents them from occupying the same region in space.

In the LDA, the exchange-correlation energy depends only on the electron density ρ at the particular coordinate where the functional is being calculated. The LDA exchange-correlation functional is given in Equation (3.31).

$$E_{xc}^{LDA}\left[\rho\right] = \int (r) \,\varepsilon_{xc}\left(\rho(\vec{r})\right) dr \tag{3.31}$$

Where, $E_{XC}^{LDA}[\rho]$ = total exchange-correlation energy, $\rho(\vec{r})$ = local electron density and $\varepsilon_{xc}(\rho(\vec{r}))$ = exchange-correlation energy per electron.

While LDA offers a computationally efficient approach, it is crucial to acknowledge its inherent limitations as an approximation. The assumption of a uniform local density can lead to inaccuracies, particularly in systems characterised by rapidly varying densities or strong electron correlations. As a result, LDA underestimates energetic barriers and overestimates binding energies, but it provides sufficiently accurate results for vibrational frequencies and molecular structures. More advanced methods, such as the Generalized Gradient Approximation (GGA), have been developed to address these limitations and provide a more nuanced description of electron interactions.⁷

3.4.3.4. Generalised Gradient Approximation (GGA)

The Generalized Gradient Approximation (GGA) is an improved improvement on the Local Density Approximation, both of which aim to estimate the exchange-correlation energy of a system, taking into account interactions between electrons that go beyond classical electrostatic considerations. While LDA assumes a locally uniform electron density at each point in space, GGA considers the spatial variations in electron density and incorporates the gradient of the electron density as an additional variable, which allows for a more accurate representation of the non-homogeneity present in real electron densities. The GGA assumes that the exchange-correlation potential depends on the density at point r and on the gradient of the density.¹⁸

$$V_{XC} = [\rho(r), \nabla \rho(r)]$$
(3.32)

Compared to LDA (Local Density Approximation), GGA methods provide better accuracy by accounting for density gradients, especially in systems where the electron density exhibits significant variations. This makes GGA suitable for broader applications in chemistry and materials science.

3.4.3.5. Non-Local Functionals

Nonlocal van der Waals (vdW) exchange-correlation functionals depend on the electron density at two separate points, r and r', in space, capturing the nonlocal nature of vdW interactions. Additionally, some functionals may incorporate the gradients of the electron density.

$$V_{XC} = \left[\rho\left(r\right), \nabla\rho(r), \rho\left(r^{1}\right), \nabla\rho\left(r^{1}\right)\right]$$
(3.33)

 $V_{XC} = [\rho(r), V\rho(r), \rho(r^{1}), V\rho(r^{1})]$ (3.33) Non-local functionals account for the correlation of electron density at multiple points in space, making them accurate for long-range interactions like van der Waals forces. They are more challenging to compute than local functionals, which only consider electron density at one point, but are more accurate in describing weak interactions. The LMKLL vdW-DF functional used in this study in SIESTA calculations is an example of a non-local functional that incorporates van der Waals interactions. In this work, other implemented functionals include both LDA and GGA types, which are suitable for varying levels of approximation. The LMKLL (vdW-DF2) functional was specifically chosen based on validation tests conducted by a group member, Dr J. Flitcroft, to ensure its reliability for the systems studied.27-28

3.5. BLOCH'S THEOREM

According to Bloch's theorem, the potential energy felt by an electron in a material undergoes periodic changes with the periodicity known as the lattice constant. The wavefunctions that describe the electron in such a periodic potential can be expressed as a product of a plane wave and a periodic function that has the same periodicity as the lattice. Essentially, this theory states that the solutions to the Schrödinger equation for a periodic potential can be expressed as plane waves that are modulated by periodic functions. In other words, the wave function can be thought of as a combination of a travelling wave and a function that repeats with the same period as the crystal lattice.²⁹

The theorem is expressed in equation (3.34).

 $\psi_k(x) = e^{ik.x} u_k(x)$ (3.34) Where, $\psi_k(x)$ is the wavefunction for a specific wavenumber k, $e^{ik.x}$ is the plane wave factor, k is the wavenumber and $u_k(x)$ is a periodic function with the same periodicity as the crystal lattice.

The Bloch theorem has several implications, including the presence of itinerant wavefunctions, which means that electrons in periodic crystals exhibit wave-like behaviour and are not localised to specific atoms. Another consequence is the formation of band structures, where the allowed energy states for electrons form bands separated by energy gaps. Additionally, the energy of an electron depends on its wavenumber within the first Brillouin zone, which is a specific range of *k*-values.

3.4. COMPUTATIONAL METHODS

3.4.1. SIESTA

SIESTA, or the Spanish Initiative for Electronic Simulations with Thousands of Atoms, is a computational software package that empowers researchers to conduct precise and efficient electronic structure calculations and simulations of molecules, solids, and surfaces. Leveraging Density Functional Theory, SIESTA is capable of performing electronic structure calculations for large numbers of atoms. Thanks to its use of order-N algorithms, SIESTA's computational cost scales linearly with system size.³⁰

SIESTA is a state-of-the-art computational tool that offers a plethora of features to its users.³¹ It employs flexible-size basis sets, using numerical atomic orbitals that allow for fast calculations with minimal basis sets and highly converged results with larger ones. The use of norm-conserving pseudopotentials ensures an accurate description of electron-ion interactions while reducing computational complexity. SIESTA also employs efficient integral evaluation methods, allowing for the calculation of two-centre integrals crucial for DFT calculations. The real-space grid approach used for evaluating potentials and matrix elements on a grid enables efficient linear scaling. Additionally, SIESTA minimises the energy functional using Wannier-like orbitals, eliminating the need for explicit wavefunction orthogonalisation and further enhancing efficiency. Lastly, SIESTA provides a non-selfconsistent but fast method for initial relaxations and exploratory simulations through the Harris functional. It enables the execution of large-scale simulations that were previously impractical due to computational limitations. Additionally, it offers a diverse range of accuracy and speed options, catering to the varying needs of simulation requirements. The framework incorporates k-point sampling, a method used to discretise the Brillouin zone and accurately capture the periodic nature of the electronic wavefunction, especially in materials like graphene. It also accounts for finitetemperature effects. Notably, SIESTA is an open-source code that is freely available for use and modification with continuous development and improvement are ongoing, with new functionalities and capabilities being added regularly.^{31,32} For this study, SIESTA is applied to obtain information regarding the electronic properties, band structures, and optical properties of graphene-based materials.

3.4.1.1. Optical Properties

SIESTA employs a two-step process to determine the optical properties of materials. Initially, a standard electronic structure calculation is conducted to ascertain the electronic ground state of the system. Next, it uses the electronic structure data to evaluate the imaginary component of the dielectric function, which characterises the material's reaction to light. This entails computing transition probabilities between energy levels and applying broadening and a scissor correction, if required. The number of energy levels included and the granularity of the calculation k-point grid influence both accuracy and computational expenditure. SIESTA provides valuable insights into the optical properties of materials via these computations.³¹

3.4.1.2. Density of States (DOS)

SIESTA can calculate the Projected Density of States (PDOS) alongside the total DOS. First, it performs a self-consistent calculation to determine the electronic ground state and obtain the Kohn-Sham eigenvalues. Then, SIESTA projects the Kohn-Sham wavefunctions onto atomic orbitals within the simulation cell, for a defined range of energies. The weight of each projected wavefunction is squared and added across all occupied states. This sum represents the contribution of the specific atomic orbitals to the total DOS at that energy point. This information is helpful in understanding the contribution of individual orbitals to the electronic structure of the material being studied.³¹

3.4.1.3. Band Structures

SIESTA is able to calculate band structures by using specified k-points in the Brillouin zone using defined lines/paths for calculating the band structure (BandLines) or specified individual k-

points for calculation (BandPoints). SIESTA performs the computation of the Kohn-Sham equations at each k-point to obtain the eigenvalues (energy levels) of electronic states. The results are stored in a dedicated file containing the k-point coordinates, corresponding band energies, and the Fermi level.³¹

3.4.2. Gaussian

The Gaussian software suite is a formidable tool for conducting electronic structure calculations on a molecular level. It includes a range of DFT and wavefunction-based methods at different levels of complexity, allowing for accurate modelling of electronic structures in a variety of contexts. It offers a range of functionalities including geometry optimisation, vibrational frequency calculations, electronic properties calculations, and thermodynamic property calculations.^{33,34}

3.5. OTHER SOFTWARE USED

3.5.1. VESTA

VESTA is a specialised 3D visualisation software that is primarily used for the analysis of crystal structures, particularly in the field of crystallography.³⁵ The figures of the graphene-based structures in this thesis are produced using VESTA.

3.5.2. Avogadro

Avogadro is a sophisticated molecular editing and visualising program that is available for free and is open source. It has been designed to enable molecular editing and visualization and provides users with the ability to construct, view, and manipulate structures in three-dimensional space. Additionally, Avogadro has a range of features that allow for basic computational chemistry tasks, including molecular mechanics geometry optimisation. ³⁶ This program has been instrumental in the construction of many of the structures calculated in this thesis.

3.5.3. Nanotube Modeler

Nanotube Modeler is a software tool designed for creating and visualising models of nanotubes, nanocones, and fullerenes.^{37,38} It was used in this study to build the mentioned 1D and 0D structures.

3.6. REFERENCES

¹ Harvey, J. (2018). *Computational chemistry*. Oxford University Press.

² Heisenberg, W. (1971). *Physics and Beyond* (p. 206). HarperCollins Publishers.

³ Stefanovich, E. (2019). *Elementary Particle Theory. Volume 1, Quantum mechanics*. De Gruyter.

⁴ Young, T. (1804). I. The Bakerian Lecture. Experiments and calculations relative to physical optics. *Philosophical Transactions of the Royal Society of London*, *94*, 1–16. <u>https://doi.org/10.1098/rstl.1804.0001</u>

⁵ Maxwell, J. C. (1864). II. A dynamical theory of the electromagnetic field. *Proceedings of the Royal Society of London*, *13*(155), 531–536. <u>https://doi.org/10.1098/rspl.1863.0098</u>

⁶ Hertz, H. (1888). Ueber die Einwirkung einer geradlinigen electrischen Schwingung auf eine benachbarte Strombahn. *Annalen Der Physik*, *270*(5), 155–170. <u>https://doi.org/10.1002/andp.18882700510</u>

⁷ Levine, I. N. (2014). *Quantum chemistry*. Pearson, Cop. [I.E.

⁸ Manjit Kumar. (2009). *QUANTUM : einstein, bohr, and the great debate about the nature of reality.* Fourth Estate Ltd.

⁹ Nauenberg, M. (2016). Max Planck and the birth of the quantum hypothesis. *American Journal of Physics*, 84(9), 709–720. <u>https://doi.org/10.1119/1.4955146</u>

¹⁰ Einstein, A. (1905). Über einen die Erzeugung und Verwandlung des Lichtes betreffenden heuristischen Gesichtspunkt. *Annalen Der Physik*, *322*(6), 132–148. <u>https://doi.org/10.1002/andp.19053220607</u>

¹¹ Atkins, P. W., De Paula, J., & Keeler, J. (2019). Atkins' Physical Chemistry (11th ed.). Oxford University Press.

¹² Rutherford, E. (1911). LXXIX. The scattering of α and β particles by matter and the structure of the atom. *The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 21*(125), 669–688. <u>https://doi.org/10.1080/14786440508637080</u>

¹³ N. Bohr Dr. phil. (1913) I. *On the constitution of atoms and molecules*, The London, Edinburgh, and Dublin Philosophical Magazine and Journal of Science, 26:151, 1-25, DOI: <u>10.1080/14786441308634955</u>

¹⁴ DE BROGLIE, L. (1923). Waves and Quanta. *Nature*, *112*(2815), 540–540. <u>https://doi.org/10.1038/112540a0</u>

¹⁵ Davisson, C., & Germer, L. H. (1927). Diffraction of Electrons by a Crystal of Nickel. *Physical Review*, *30*(6), 705–740. <u>https://doi.org/10.1103/physrev.30.705</u>

¹⁶ Planck, M. (1901). Ueber das Gesetz der Energieverteilung im Normalspectrum. *Annalen Der Physik*, *309*(3), 553–563. <u>https://doi.org/10.1002/andp.1901309031</u>

¹⁷ Schrödinger, E. (1926). Quantisierung als Eigenwertproblem. *Annalen Der Physik*, 384(4), 361–376. https://doi.org/10.1002/andp.19263840404

¹⁸ Jensen, F. (2017). *Introduction to computational chemistry*. New Jersey John Wiley & Sons Inc.

¹⁹ Schroeder, D. V. (2022). *Notes on Quantum Mechanics*. Weber State University.

²⁰ Jecko, T. (2013). On the mathematical treatment of the Born-Oppenheimer approximation. *Journal of Mathematical Physics, 55*, 053504.

²¹ Pisana, S., Lazzeri, M., Casiraghi, C., Novoselov, K. S., Geim, A. K., Ferrari, A. C., & Mauri, F. (2007). Breakdown of the adiabatic Born–Oppenheimer approximation in graphene. *Nature Materials*, *6*(3), 198–201. <u>https://doi.org/10.1038/nmat1846</u>

²² Atkins, P. W., & Friedman, R. (2005). *Molecular quantum mechanics* (4th ed.). Oxford University Press.

²³ Pauli, W. (1925). Über den Zusammenhang des Abschlusses der Elektronengruppen im Atom mit der Komplexstruktur der Spektren. *Zeitschrift Für Physik*, *31*(1), 765–783. <u>https://doi.org/10.1007/bf02980631</u>

²⁴ Sherrill, C. D. (n.d.). An Introduction to Hartree-Fock Molecular Orbital Theory [Review of An Introduction to Hartree-Fock Molecular Orbital Theory]. School of Chemistry and Biochemistry Georgia Institute of Technology. http://vergil.chemistry.gatech.edu/notes/hf-intro.pdf

²⁵ Slater, J. C. (1929). The Theory of Complex Spectra. *Physical Review*, *34*(10), 1293–1322. <u>https://doi.org/10.1103/physrev.34.1293</u>

²⁶ Koch, W., & Holthausen, M. C. (2015). *A Chemist's Guide to Density Functional Theory*. Wiley-VCH.

²⁷ Lee, K., Murray, É. D., Kong, L., Lundqvist, B. I., & Langreth, D. C. (2010). Higher-accuracy van der Waals density functional. *Physical Review B*, *82*(8). <u>https://doi.org/10.1103/physrevb.82.081101</u>

²⁸ Artacho, E., María, J., Barcelona, C., Center, S., Gale, J., García, A., Junquera, J., Martin, R., Papior, N., & Soler, J. (2021). <u>https://siesta-project.org/SIESTA_MATERIAL/Docs/Manuals/siesta-4.1.5.pdf</u>

²⁹ Grosso, G., & Giuseppe Pastori Parravicini. (2013). *Solid State Physics*. Academic Press.

³⁰ Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., & Sánchez-Portal, D. (2002). The SIESTA method for*ab initio*order-Nmaterials simulation. *Journal of Physics: Condensed Matter*, *14*(11), 2745–2779. https://doi.org/10.1088/0953-8984/14/11/302

³¹ Artacho, E., María, J., S., Gale, J., García, A., Junquera, J., Martin, R., Papior, N., & Soler, J. (2021). <u>https://siesta-project.org/SIESTA_MATERIAL/Docs/Manuals/siesta-4.1.5.pdf</u>

³² García, A., Papior, N., Akhtar, A., Artacho, E., Blum, V., Bosoni, E., Brandimarte, P., Brandbyge, M., Cerdá, J. I., Corsetti, F., Cuadrado, R., Dikan, V., Ferrer, J., Gale, J., García-Fernández, P., García-Suárez, V. M., García, S., Huhs, G., Illera, S., & Korytár, R. (2020). Siesta: Recent developments and applications. *The Journal of Chemical Physics*, *152*(20), 204108. <u>https://doi.org/10.1063/5.0005077</u>

³³ GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

³⁴ Frisch, M. J., Trucks, G. W., Schlegel, H. B., Scuseria, G. E., Robb, M. A., Cheeseman, J. R., Scalmani, G., Barone, V., Petersson, G. A., Nakatsuji, H., Li, X., Caricato, M., Marenich, A. V., Bloino, J., Janesko, B. G., Gomperts, R., Mennucci, B., Hratchian, H. P., Ortiz, J. V., Izmaylov, A. F., Sonnenberg, J. L., Williams-Young, D., Ding, F., Lipparini, F., Egidi, F., Goings, J., Peng, B., Petrone, A., Henderson, T., Ranasinghe, D., Zakrzewski, V. G., Gao, J., Rega, N., Zheng, G., Liang, W., Hada, M., Ehara, M., Toyota, K., Fukuda, R., Hasegawa, J., Ishida, M., Nakajima, T., Honda, Y., Kitao, O., Nakai, H., Vreven, T., Throssell, K., Montgomery, J. A., Peralta, J. E., Ogliaro, F., Bearpark, M. J., Heyd, J. J., Brothers, E. N., Kudin, K. N., Staroverov, V. N., Keith, T. A., Kobayashi, R., Normand, J., Raghavachari, K., Rendell, A. P., Burant, J. C., Iyengar, S. S., Tomasi, J., Cossi, M., Millam, J. M., Klene, M., Adamo, C., Cammi, R., Ochterski, J. W., Martin, R. L., Morokuma, K., Farkas, O., Foresman, J. B., & Fox, D. J. (2016). *Gaussian 16* (Revision C.01). Gaussian, Inc.

³⁵ Momma, K., & Izumi, F. (2011). VESTA 3 for three-dimensional visualization of crystal, volumetric and morphology data. *Journal of Applied Crystallography*, 44(6), 1272–1276. https://doi.org/10.1107/s0021889811038970
³⁶ Hanwell, M. D., Curtis, D. E., Lonie, D. C., Vandermeersch, T., Zurek, E., & Hutchison, G. R. (2012). Avogadro: an advanced semantic chemical editor, visualization, and analysis platform. *Journal of Cheminformatics*, *4*(1). <u>https://doi.org/10.1186/1758-2946-4-17</u>

³⁷ Melchor, S., & Dobado, J. A. (2004). CoNTub: An Algorithm for Connecting Two Arbitrary Carbon Nanotubes. *Journal of Chemical Information and Computer Sciences*, *44*(5), 1639–1646. https://doi.org/10.1021/ci049857w

³⁸ Johnson, J. E., & Speir, J. A. (1997). Quasi-equivalent viruses: a paradigm for protein assemblies. *Journal of Molecular Biology*, *269*(5), 665–675. <u>https://doi.org/10.1006/jmbi.1997.1068</u>

4. Optoelectronic Properties and Characterisation of Graphene and Aerosol Gel Graphene Films

CONTENTS

List of Figures	105
List of Tables	108
Abbreviations	109
Overview	110
4.1. Sample Set 1: Graphene and Oxygen-Containing Aerosol Gel Graphene Films w thickness	ith Different 111
Disclaimer	111
4.1.1. Sample Description	111
4.1.1.1. Preparation of the Graphene and Oxygen-Containing Aerosol Gel Graphene Fi	lms 111
4.1.2. Characterisation Methods	112
4.1.2.3. X-ray photoelectron spectroscopy (XPS)	112
4.1.2.4. Scanning Electron Microscopy (SEM)	112
4.1.2.1. Steady State Spectroscopy (UV-Vis)	112
4.1.2.2. Ultrafast Transient Absorption (TA) Spectroscopy (Pump-Probe Spectroscop	oy)112
Data Analysis	113
4.1.2.5. Atomic force microscopy (AFM)	113
4.1.3. Results	113
4.1.3.1. XPS	113
4.1.3.2. SEM	114
4.1.3.3. UV-VIS Steady State	114
4.1.3.4. Transient Absorption Spectroscopy	115
Graphene I, II and III	116
The optoelectronic response of graphene upon excitation with 400 nm light	118
Extended Time Window	119
Power Dependence Study	122
Aerogel Graphene (AG) I, II and III	125
Longer Time Window Experiments	126
Comparison of Graphene and Aerogel Samples	128
Initial Lifetimes	128
Power dependence comparison of AG III and G III	129
Summary and Discussion of Pump-Probe Results	130
4.1.4. Discussion	130
4.2. SAMPLE SET 2: AEROGEL GRAPHENE FILMS WITH VARYING OXYGEN CONTENT KAPTON TAPE SUBSTRATE	PRINTED ON 132
4.2.1. Sample Description	132
4.2.2. Characterisation Methods	

4.2.2.3. Pump-Probe Spectroscopy	132
4.2.2.1. FTIR	132
4.2.2.2. XPS	132
4.2.2.4. AFM	132
4.2.3. Results	132
4.2.3.1. Transient Absorption Results	132
Transient Absorption in Transmittance Mode	132
Lower Oxygen Content AG Film 0.3 on Kapton Tape	132
A Higher Oxygen Content, 0.75 AG, on Kapton Tape	134
Influence of Oxygen Content on Carrier Decay in AG 0.3 and AG 0.75 on Kapton	136
Kinetics Lifetimes of all Diluted AG on Kapton Samples	136
Transient Absorption in Reflectance Mode	137
Disclaimer	141
4.2.3.2. FTIR	141
XPS of AG samples on Kapton	144
4.2.3.4. AFM	148
4.2.4. Discussion	148
4.3. Sample Set 3: diluted Graphene and Aerogel Graphene with Varying Oxygen Conte QuartZ	ent Printed on 149
4.3.1 Sample Description	149
4.3.2 Characterisation Methods	149
4.3.2.1. Scanning Electron Microscopy (SEM)	149
4.3.2.2. Transmission Electron Microscopy (TEM)	149
4.3.2.3. UV-Vis Spectroscopy	149
4.3.2.4. Pump-Probe Spectroscopy (UV and NIR)	149
4.3.2.5. Surface and Depth Analysis: X-ray Photoelectron Spectroscopy (XPS)	149
4.3.2.6. Surface Analysis: Profilometry	149
4.3.2.7. Material Characterisation: Scanning Near-Field Infrared Microscopy (SNON Force Microscopy (AFM)	l) with Atomic 150
4.3.2.8. Raman Spectroscopy	150
4.3.3. Results	150
4.3.3.1. SEM	150
4.3.3.2. TEM	151
4.3.3.3. UV-VIS	152
Estimated Band Gaps via Tauc Plots	154
4.3.3.4. Transient Absorption Spectroscopy Results	155
Kinetic Traces, UV and NIR	156

Magnitude of the Long-Lived Signal	
Lifetimes and Recovery at Different Wavelengths	
Power Dependence Study for Sample AG 0.75 at 525nm (UV)	
4.3.3.5. XPS Results	
4.3.3.6. Profilometer	
4.3.3.7. SNOM and AFM	
4.3.3.8. RAMAN	
4.3.4. Discussion	
4.4. Sample Set 4: Samples with Higher Oxygen Content	
4.4.1. Sample Description	
4.4.2. Characterisation Methods	
4.4.3. Results	
4.4.3.1. UV-VIS Results	
4.4.3.2. Transient Absorption Spectroscopy Results	
4.4.3.3. X-ray Photoelectron Spectroscopy (XPS)	
4.4.4. Discussion	
4.5. Conclusion	
4.7. References	

LIST OF FIGURES

Figure 4.1. XPS Characterisation of G III, Survey Spectrum (left) and C 1s Peak Fitting (right), note: 'Data 'refers to the overall extracted raw data.

Figure 4.2. SEM Images of G I and AG I Films (X35.0k, 5.0kV)

Figure 4.3. The UV-Vis Transmission Spectra of Graphene (left) and Aerogel (right) I, II and III on Quartz, in the Range 200 - 800 nm. The spectrum of the quartz substrate only is also shown (black and purple), at room temperature.

Figure 4.4. Change in Transmission ($\Delta T/T$) of all G (top row) and all AG (bottom row) Samples, Following Excitation at 400 nm, in the Spectral Range 440–680 nm, from –100 to 750 fs.

Figure 4.5. (top) Transient Change in Transmission of One, Two and Three-Pass Printed Graphene on Quartz, Following Excitation at 400 nm, from 40 fs to 1200 fs (data cropped to ~800fs), at Room Temperature, (bottom) Kinetic Analysis of All Graphene Samples.

Figure 4.6. Transient Change in Transmission Kinetics of One-Pass Printed Graphene on Quartz, Following Excitation at 400 nm.

Figure 4.7. Kinetics Traces at 475 nm (black), 525 nm (red) and 575 nm (blue) for Graphene I, II and III Following Excitation at 400 nm.

Figure 4.8. Plots of the Lifetimes of the 'Fast' and 'Slow' Decays of Graphene I, II and III Against Probe Photon Wavelength. Associated errors are shown as error bars.

Figure 4.9. (left) Power Dependence Kinetic Fitting at 540 nm for the G I Sample, and (right) Power Dependence Kinetic Fitting at 560 nm for the G II Sample.

Figure 4.10. Power-Dependent Lifetime Analysis of Graphene III Film at Different Wavelengths

Figure 4.11. Lifetime vs Beam Power (Fluence) Plots of GI, GII, GIII.

Figure 4.12. (top) Transient Change in Transmission of One-Pass Printed Aerogel Graphene on Quartz, Following Excitation at 400 nm, from 20-40 fs to 1080-1200 fs, at Room Temperature, (bottom) Kinetic Analysis of all AG Samples.

Figure 4.13. Kinetics Traces at Wavelengths Ranging from 500 nm to 600 nm for AG I, II and III Following Excitations at 400 nm. The solid traces overlaid are analytic fits using a sum of three or four exponential decays convolved with a Gaussian function.

Figure 4.14. Comparing the Initial Decay Lifetimes of G vs AG After Photoexcitation Dynamics Across Wavelengths Taken from the Short Time Window Experiments.

Figure 4.15. Power Dependence of Excited State Lifetimes in G III and AG III

Figure 4.16. Transient Absorption Study of (lowest oxygen content) AG 0.3 Film Printed on Kapton Tape After 400 nm Excitation (1.0 mW).

Figure 4.17. Transient Absorption Study of AG 0.75 Film with the Highest Oxygen Content Printed on Kapton Tape After 400 nm Excitation (1.0 mW).

Figure 4.18. Initial Ultrafast Recovery Lifetime vs Wavelength for AG/Kapton Samples.

Figure 4.19. Combined Kinetics of Early and Late Lifetimes of AG Printed on Kapton Samples: (left) Early Time Study, (right) Cropped Late Time Study, Both at 550 nm, with the Full Data given in the Inset.

Figure 4.20. Kinetics Fittings of Early Time and Late Time Reflectance Experiments Against Transmittance Experiments of Samples AG 0.3 (left) AG 0.4 (right), the Black Lines are all T and the Coloured Lines Represent R.

Figure 4.21. Transient Change in Transmission of Sample AG 0.4 Following Excitation at 400 nm.

Figure 4.22. Kinetic Fitting at 550 nm for the Early time Window Experiments for Samples AG 0.3, 0.4 and 0.5 in Both Reflectance and Transmittance Mode Following Excitation at 400 nm at Room Temperature.

Figure 4.23. FTIR Spectra of Kapton, AG 0.5 (Annealed and Unannealed), and AG 0.75 (Annealed and Unannealed)

Figure 4.24. The Chemical Structures of Kapton (1), Ethylcellulose (2), Terpineol (3) and Cyclohexanol (4)

Figure 4.25. The FTIR Spectrum of AG 0.5 and AG 0.75 Flakes Were Removed from Kapton and Analysed Using ATR.

Figure 4.26. XPS Analysis of Carbon Bonding of Kapton Tape, note: 'Data 'refers to the overall extracted raw data.

Figure 4.27. XPS Analysis of Bonding C 1s Peaks in AG Films With Varying Oxygen Content of All the Annealed Samples.

Figure 4.28. XPS Analysis of Bonding 1s Peaks in AG Films with Varying Oxygen Content (Unannealed)

Figure 4.29. SEM Images of G and AG Samples. All Images have the same magnification and resolution for clear comparison.

Figure 4.30. TEM Images of all AG Samples and 1 G Sample All Images Have the Same Resolution.

Figure 4.31. UV-vis Transmission Spectra of Ink-Jet Print Aerosol Gel Graphene Films, with Varying O/C Ratio, and a Pristine Graphene Film (left). Normalised Graph of the UV-Vis Absorption Spectra (right).

Figure 4.32. (a) UV-Vis Absorbance Comparison of Samples from Batch 1 and Batch 3, (b) Comparison of Absorbance on Sample AG 0.75 at Different Positions of the Film

Figure 4.33. Tauc Plots for Batch 3 AG Samples Printed on Quartz, Showing the Estimated Band Gaps Calculated Using the Indirect Bandgap Method.

Figure 4.34. (left) Graphs Depict the Dependence of Carbon-Optical Phonon (C-OP) Scattering Rates on the Wavelength of the Incident Probe Light. (right) Transient Changes in Transmission (Δ T/T) of G and AG 0.3–0.75, Following Excitation at 400 nm, in the Spectral Regions 420–690 nm and 850–1600 nm. Pump-probe time delays span -100 to 1500 fs.

Figure 4.35. Normalised Single Point Kinetic Traces at 550 nm (left) and 1550 nm (right), for All Samples, Overlaid with their Exponential Fits.

Figure 4.36. Kinetics Traces at 550 nm, Both Normalised (right) and Unnormalised (left), Highlighting the Recovery Dynamics of the Negative $\Delta T/T$ Signal.

Figure 4.37. Fluence Dependence of Excited State Lifetime in Aerosol Gel Graphene 0.75 Film (right) Zoomed in to 0 - 4 ps.

Figure 4.38. XPS of all AG Samples with Varying Oxygen Content. Orange Graphs Depict the Carbon Fitting, and the Blue and Green Graphs Show the Fitting of Oxygen and Silicon, Respectively. (a) AG 0.3, (b) AG 0.4, (c) AG 0.5 and (d) AG 0.75.

Figure 4.39. Raman Spectroscopy Measurements of the AG Samples with O/C Ratio of 0.3, 0.4, 0.5 and 0.75 after Annealing. 35

Figure 4.40. Carrier Relaxation in Graphene Under Ultrafast Light Pulses.

Figure 4.41. The UV-Vis Absorption Spectra of AG 0.6 and AG 0.85 Compared to Graphene and AG 0.75 at Room Temperature.

Figure 4.42. The Ratio of the Preexponential Factors, A^{∞} and A1, as a Function of O/C of the Aerosol Gel Films. O/C of the pure graphene film is defined as 0.

Figure 4.43. XPS Analysis of C 1s Binding Energies in Graphene ink (left) and AG ink (right) with Ethyl Cellulose Surfactant.

Figure 4.44. XPS Analysis of C 1s Binding Energies in Graphene Film (left) and AG Film (right)

LIST OF TABLES

Table 4.1 Optical Properties of Graphene and AG Films

Table 4.2 Lifetimes of Graphene samples (from 40 fs to 1200 fs)

Table 4.3 Lifetimes extracted from triexponential fits of $\Delta T/T$ Spectra at 475 nm, 525 nm, and 575 nm for graphene samples.

Table 4.4 Tabulated data for the power dependence kinetic fitting at 540 nm for G I

 Table 4.5 Tabulated data for the power dependence kinetic fitting at 560 nm for G II sample.

Table 4.6 Tabulated data of the impact of excitation power on relaxation processes in Graphene III

 Film

Figure 4.7 Kinetics Traces at 475 nm (black), 525 nm (red) and 575 nm (blue) for Graphene I, II and III Following Excitation at 400 nm. The solid traces overlaid are analytic fits using a sum of three exponential decays convolved with a Gaussian function.

Table 4.8 Extracted decay timescales from AG photoexcitation kinetics (λ = 500-600 nm, 400 ps)

Table 4.9 Repeated and revised decay timescales for AG I photoexcitation kinetics (λ = 500-600 nm, 400 ps)

Table 4.10 Tabulated data for the power dependence kinetic fitting at 550 nm for G III

 Table 4.11
 Tabulated data for the power dependence kinetic fitting at 550 nm for AG III sample

Table 4.12 Early Time Kinetics of AG 0.3 on Kapton (35-670 fs)

Table 4.13 Late Time Kinetics of AG 0.3 on Kapton (0.6 ps - 400 ps)

Table 4.14 Early Time Kinetics of AG 0.75 on Kapton (45-750 fs)

 Table 4.15
 Late Time Kinetics of AG 0.75 on Kapton (0.7 ps - 400 ps)

Table 4.16 Comparison of Reflectance and Transmittance (Late Time) Lifetimes for AG 0.3 to 0.5samples at 550 nm

 Table 4.17
 Table of IR absorption

Table 4.18 XPS fitting of the % Carbon according to C 1s binding energies (eV) of all AG samples andKapton.

Table 4.19 Optical Properties of Batch 3 Samples

Table 4.20 Lifetimes of all samples at 550 nm (UV-Vis)

 Table 4.21 Lifetimes of all samples at 1550 nm (NIR)

Table 4.22 Wavelength-Dependent Recovery Lifetime in Graphene and AG 0.3-0.75

Table 4.23 XPS Binding Energies (eV) for Carbon, Oxygen, and Silicon for AG samples

Table 4.24 Maximum and Average Height of Thin AG Film Samples

Table 4.25 Optical properties of batch 4 samples

Table 4.26 Lifetimes of AG 0.6 and AG 0.85 samples from batch 4 compared to the lifetimes of graphene and AG 0.75 from batch 3 at 550 nm (UV-Vis)

ABBREVIATIONS

AFM	Atomic Force Microscopy
AG	Aerogel / Aerosol gel Graphene
ATR	Attenuated Total Reflectance
FTIR	Fourier Transform Infrared Spectroscopy
FWHM	Full Width at Half Maximum
G	Graphene
GO	Graphene Oxide
IR	Infrared Spectroscopy
IRF	The instrument response function
rGO	Reduced Graphene Oxide
SEM	Scanning Electron Microscopy
SNOM	Scanning Near-Field Optical Microscopy
ТА	Thermal Analysis
ТЕМ	Transmission Electron Microscopy
TwBLG	Twisted Bilayer Graphene
UV Vis	Ultraviolet-Visible Spectroscopy
XPS	X-ray Photoelectron Spectroscopy

Optoelectronic Properties and Characterisation of Graphene and Aerosol Gel Graphene Films

OVERVIEW

Graphene films were produced at Kansas State University (KSU) for sensor devices, and four sample sets were analysed in this PhD project. Sample set 1 comprised graphene and oxygen-containing aerosol gel graphene films with varying numbers of printed layers. Sample set 2 included aerogel graphene films with different oxygen contents printed on Kapton tape substrates. Sample set 3 involved diluted graphene and aerogel graphene films with varying oxygen contents, printed on quartz substrates. Sample set 4 focused on films with higher oxygen content to study its effects on film properties. The group of Prof. Suprem Das at KSU produced the graphene films as part of this collaborative research.

4.1. SAMPLE SET 1: GRAPHENE AND OXYGEN-CONTAINING AEROSOL GEL GRAPHENE FILMS WITH DIFFERENT THICKNESS

The overall aim of studying these samples was to understand the optoelectronic properties and surface characteristics of the graphene materials. Specifically, the printed aerogel graphene ink was compared to standard graphene ink films, and the effects of the increasing number of layers were observed in this section.

The primary goal was to measure the transient change in light transmission of the various graphene samples when exposed to light pulses with wavelengths ranging from 400 to 800 nm to follow the charge carriers' dynamics near the bandgap. Charge carriers' dynamics was investigated by varying the pump pulse energy, fluence (intensity), and probe pulse energy used in the measurements. X-ray photoelectron spectroscopy, electron microscopy and Raman spectroscopy were also employed to obtain complementary data about the graphene and aerosol gel graphene samples' surface composition and chemical bonding.

Disclaimer

The results presented in this section were published in *J. Phys. Chem. C* 2022, 126, 18, 7949–7955 "Ultrafast Transient Absorption Spectroscopy of Inkjet-Printed Graphene and Aerosol Gel Graphene Films: Effect of Oxygen and Morphology on Carrier Relaxation Dynamics" by A. J. Auty, N. Mansouriboroujeni, T. Nagaraja, D. Chekulaev, C. M. Sorensen, S. R. Das, N. Martsinovich, A. A. P. Chauvet.¹

4.1.1. Sample Description

4.1.1.1. Preparation of the Graphene and Oxygen-Containing Aerosol Gel Graphene Films

All the graphene-based material films analysed in this chapter were prepared by the team of Prof. Suprem Das at the Department of Industrial and Manufacturing Systems Engineering at Kansas State University.² Two types of inks, graphene ink (G) and aerosol gel graphene (AG) ink, were synthesized by the group of S. Das, Kansas State University, using a high-shear force process.³

For the graphene ink, commercially available graphene powder from Millipore Sigma was used as the starting material. In the case of AG ink, the precursor material was generated through a gas-phase co-detonation process involving hydrocarbons and oxygen. The large-scale production of graphene aerosol gel was achieved via a controlled detonation method using acetylene (C_2H_2) and oxygen (O_2) in a multiliter chamber.^{3,4}

The graphene aerosol gel samples (in powder form) consisted of pristine graphene nanosheet aggregates loosely bound together to form a macroscopic gel. To prepare the aerosol gel ink, the graphene aerosol gel powder (250 mg) was dispersed in 50 mL of ethanol and mixed with 1 w/v% ethyl cellulose (EC, Sigma-Aldrich, 4 cP grade measured in 80:20 toluene: ethanol at 5 wt %, 48% ethoxy) as an emulsifier. The suspension was filtered through a 5- μ m glass fibre syringe filter to remove larger particles. To flocculate the suspension, NaCl aqueous solution (0.04 g/mL in deionized water) was added, followed by vacuum filtration using a 0.45- μ m nylon filter. A high-shear force was applied for 30 minutes using an ultrasonic probe (500 W, 20 kHz, Q500 sonicate, USA), kept within an ice bath. The obtained graphene aerosol gel/ethyl cellulose paste was dried on a hot plate at 70 °C for several hours. The graphene aerosol gel ink was prepared finally by suspending the graphene aerosol gel/ethyl cellulose powder homogeneously in cyclohexanone and terpineol (volume ratio of 85:15) through bath sonication at a concentration of 70 mg/mL.⁴

For the graphene-ethyl cellulose ink, a rigorous 3-hour mixing process was followed, producing an ink with a composition of 50% weight fraction of ethyl cellulose at a concentration of 5 mg/mL in an organic solvent. Similarly, the aerosol-ethyl cellulose ink was prepared following the same protocol,

with a 3-hour mixing time and a 50% weight fraction of ethyl cellulose. A key difference between the inks was the oxygen-to-carbon (O/C) ratio of 0.5 in the precursor materials of the aerosol gel ink.⁴

Following synthesis, both inks underwent a heat treatment known as annealing. The annealing conditions, including temperature and time, were not explicitly provided in the received data. If this information was withheld due to intellectual property restrictions, it must be noted that related samples in the literature from the same group were treated comparably, typically involving drying at 70 °C for several hours.^{3,4}

The inks were inkjet-printed onto quartz substrate films in square-shaped printed patterns (0.5 cm \times 0.5 cm). Each ink type was used to create three samples with varying thicknesses, achieved by controlling the number of printing passes. The samples were labelled as G I, G II, and G III for graphene and AG I, AG II, and AG III for aerosol gel/aerogel, respectively. The numbering system corresponds to the number of printing passes, with higher numbers indicating increased film thickness from one to three printed layers. The printed samples on quartz substrates were sent for analysis to Sheffield from Kansas State University.^{1,2}

4.1.2. Characterisation Methods

4.1.2.3. X-ray photoelectron spectroscopy (XPS)

The XPS experiments were conducted at the Sheffield Surface Analysis Centre.⁵ The sample analysed was G III, consisting of three layers of pristine graphene flakes printed on quartz crystals. The decision to analyse only G III was based on its thickness, which minimises substrate interference, and the assumption of consistent composition among the graphene layers GI, GII, and GIII. The analysis areas were chosen based on the homogeneity of the graphene film. The expected elements to be identified were carbon (C), the primary element of graphene, silicon (Si) from the underlying quartz crystal (SiO₂), and oxygen (O) potentially present in the sample and originating from the substrate, contamination or surface oxides. Data collection involved a survey scan, high-resolution C 1s peak analysis, high-resolution O 1s peak analysis, and a high-resolution Si 1s peak analysis for completeness.

4.1.2.4. Scanning Electron Microscopy (SEM)

Scanning electron microscope imaging was performed at Kansas State University to examine printed graphene and graphene aerosol gel films. The microscope was a KU 8230, and the accelerating voltage was 5.0 kV.⁶

4.1.2.1. Steady State Spectroscopy (UV-Vis)

Steady-state UV-visible absorption measurements were taken using an Agilent Cary 60 UV-vis spectrometer.⁷

4.1.2.2. Ultrafast Transient Absorption (TA) Spectroscopy (Pump-Probe Spectroscopy) The experiments were conducted at the Lord Porter Ultrafast Laser Laboratory (ULS) using a Helios system (HE-VIS-NIR-3200) from Ultrafast Systems for spectroscopy in the ultraviolet-visible region.⁸

A Ti:sapphire regenerative amplifier (Spitfire Ace PA-40) provided the foundation of the laser source. It generated 800 nm pulses with a duration of 40 femtoseconds (fs) at a repetition rate of 10 kHz and an energy of 1.2 microjoules (μ). The 400 nm pump pulses were obtained by frequency doubling the amplifier's fundamental output via a BBO crystal. These pulses had a repetition rate of 2.5 kHz and an energy of 0.2 μ . The pump pulse was focused onto the sample film, creating a beam diameter of about 275 micrometres (μ m). For the fluency-dependent experiments, the energy of the pump ranged from 0.02 to ~0.3 μ J. A white light probe continuum spanning 440-710 nm was generated using a crystal and a portion of the amplifier's fundamental pulse; for short-term experiments, a CaF2 crystal was employed, while a sapphire crystal was utilised for long-term measurements. Although both crystals are capable of conducting thermal analysis experiments for both short and long durations, they emit slightly different spectra of white light. A CMOS camera measured the intensity of the probe

light transmitted through the sample with a resolution of 1.5 nm. Before generating the white light, the 800 nm pulses were directed through a computer-controlled optical delay line (DDS300, Thorlabs). The instrument response function was estimated to be around 100 fs based on the transient signal from the quartz substrate.

Data Analysis

All steady-state and time-resolved data were processed using OriginPro software. OriginPro 2019 and OriginPro 2023b were utilised for the data analysis.⁹ The pump-probe data were pre-processed using Surface Xplorer Version 4.2¹⁰ provided by Ultrafast Systems. Kinetic traces from the pump-probe data were fitted in OriginPro using a combination of decaying exponential functions and a Gaussian function. The Gaussian function accounted for the instrument response's influence on the rise time of the transient signal. The kinetic fitting function is given in the appendix.

4.1.2.5. Atomic force microscopy (AFM)

AFM was employed to acquire high-resolution images and measure the height profiles of the G III sample surface. The Bruker Multimode 5 AFM operated in soft tapping mode, utilising Bruker OTESPA-R3 cantilevers for data collection.¹¹ Gwyddion¹² software was then used to process the obtained data.

4.1.3. Results

4.1.3.1. XPS

XPS was used to characterise the composition of the samples. In Figure 4.1, the left side shows the total XPS survey of the G III film, providing a broad spectrum of all elements present in the sample. On the right side, a high-resolution XPS spectrum focuses on the carbon (C 1s) peak, where the fitting distinguishes between different carbon bonding configurations. The high carbon content indicates the presence of carbon-to-carbon single and double bonds, characteristic of graphene, with binding energies around 285 eV. Additionally, a weaker oxygen (O 1s) peak suggests the presence of oxygen atoms on the surface of the graphene film. This presence of oxygen may also be attributed to surface contamination, potentially due to environmental exposure. It is also possible that the oxygen originates from the SiO₂ substrate, as the graphene film is printed on quartz.

The XPS spectra of all graphene samples showed remarkably similar carbon fittings, indicating a consistent composition across the samples. Therefore, only the XPS of the thickest sample is shown here. In section 4.2, the XPS of G films and AG films are compared.



Figure 4.1. XPS Characterisation of G III, Survey Spectrum (left) and C 1s Peak Fitting (right), note: 'Data 'refers to the overall extracted raw data.

4.1.3.2. SEM

Figure 4.2 displays Scanning Electron Microscopy images of the graphene and aerogel graphene inks. The SEM image of the graphene film shows a predominantly smooth and uniform surface, indicating a quasi-continuous and two-dimensional (2D) structure. This smooth morphology is a characteristic of pristine graphene films, where individual graphene flakes merge to form a large, uninterrupted structure.

In contrast, the aerogel graphene (AG) film exhibits a notably different morphology. The SEM image reveals the presence of numerous smaller, three-dimensional particles. These particles appear packed, indicating a more heterogeneous structure than the graphene film. The introduction of oxygen during the production of the aerogel graphene ink may disrupt the stacking and alignment of individual graphene flakes, resulting in a more folded or crumpled structure. It can be concluded that the presence of oxygen causes the formation of smaller flakes and particles in the ink.



Graphene

Aerogel Graphene

Figure 4.2. SEM Images of G I and AG I Films (X35.0k, 5.0kV)

4.1.3.3. UV-VIS Steady State

This study examined the optical transmission properties of graphene and aerogel graphene films prepared through inkjet printing. The influence of film thickness on transmission spectra was analysed for samples prepared using 1, 2, and 3 printing passes, as shown in Figure 4.3. Both graphene and AG films exhibit broad light absorption across the 200-800 nm spectral range. Graphene films display a distinct minimum in their transmission spectra at approximately 267 nm. This minimum is attributed to the recognised $\pi \rightarrow \pi^*$ electronic transition within the graphene lattice, as documented by previous literature.¹³ AG films also exhibit broad absorption within the same spectral region. However, compared to graphene, the minimum in the AG film transmission spectra is broadened and exhibits a blue shift, with the peak position located around 247 nm. This blue shift is consistent with observations reported for graphene oxide compared to reduced graphene oxide, suggesting the presence of oxygen functional groups in the AG films.¹⁴ The broadening of the absorption peak in AG films may be due to a combination of factors. One possible factor is the presence of oxygen functionalities, which is indicated by the blue shift. Another contributing factor may be the unique 3D structure of AG films, which is different from the flatter and more planar structure of graphene.



Figure 4.3. The UV-Vis Transmission Spectra of Graphene (left) and Aerogel (right) I, II and III on Quartz, in the Range 200 - 800 nm. The spectrum of the quartz substrate only is also shown (black and purple), at room temperature.

Prior research suggests that a single graphene layer absorbs approximately 2.3% of incident white light.¹⁵ Table 4.1 also presents the estimated number of graphene and AG layers within the printed films. Table 4.1 demonstrates a positive correlation between the estimated number of printing passes and film thickness. As the table shows, this translates to a decreasing trend in overall light transmission as film thickness increases. This observation aligns perfectly with the expected behaviour for increasingly dense materials. As the film thickness increases, a more significant portion of the incident light is absorbed due to the increased material volume.

It is important to acknowledge that the number of layers is estimated based on absorption data, which itself is influenced by film thickness. However, the observed positive correlation between printing passes and the estimated number of layers is consistent with the observation of decreasing light transmission with thicker films. This finding reinforces the notion that increasing the number of printing passes leads to greater film thickness and, consequently, a higher degree of light absorption.

Sample	λmax	%T (λmax)	%T (800 nm) Number of e graphene	
GI	267	54	84.4	7
G II	265	37	75.6	12
G III	264	31	71.6	14
AG I	256	60	85.9	7
AG II	247	28	62.6	20
GA III	244	9.3	52.4	28

Table 4.1 Optical Properties of Graphene and AG Films

4.1.3.4. Transient Absorption Spectroscopy

Transient absorption spectroscopy investigated the ultrafast dynamics of photoexcited states in graphene (G) and (AG) films. Exciting the samples with a 400nm laser generated a high density of charge-separated states, allowing for a detailed study of their electronic properties.

The heatmaps in Figure 4.4 illustrate the changes in transmission for G and AG films following 400nm excitation. The x-axis represents the wavelength of light, while the y-axis represents the time delay after excitation. The colour scale indicates the magnitude and sign of the transmission change. Positive values indicate increased transmission, suggesting that electrons have transitioned to higher energy states and are less likely to absorb light at specific wavelengths. Conversely, negative values indicate a decrease in transmission, possibly due to the formation of transient species or excited states that absorb light.

The results indicate a general increase in transmission (positive $\Delta T/T$) for both G and AG samples across most of the measured spectrum. This is likely attributed to the laser pulse exciting electrons in the materials to higher energy states, making them less likely to transmit light at specific wavelengths. Additionally, all G and AG samples exhibit some recovery in transmission over time.



Figure 4.4. Change in Transmission (ΔT/T) of all G (top row) and all AG (bottom row) Samples, Following Excitation at 400 nm, in the Spectral Range 440–680 nm, from –100 to 750 fs.

Graphene I, II and III

In Figure 4.5, the $\Delta T/T$ spectra for three samples of graphene, labelled G I, II, and III, are presented. These spectra were obtained following excitation at a wavelength of 400 nm and are accompanied by kinetic traces illustrating the change in normalised transmittance over time, measured in femtoseconds, for various probe wavelengths. Additionally, the extracted lifetimes for these measurements are provided in Table 4.2.

Upon excitation at 400 nm, all three graphene samples exhibited a positive $\Delta T/T$ signal within the 430-680 nm spectral range. This signal reached a peak at approximately 40 femtoseconds (fs) and subsequently decayed monoexponentially throughout the entire spectral range, resulting in a negative $\Delta T/T$ signal. Due to the instrument's temporal resolution of approximately 150 fs, the initial peak's exact timing is unreliable. However, the rapid rise suggests a fast-occurring process upon excitation. The negative $\Delta T/T$ signal remained relatively constant over the time span shown (-22 to 800 fs), indicating minimal fluctuation in its intensity. The lifetime of the negative signal was observed to be dependent on probe wavelength. Signals with longer probe wavelengths (lower energy) decayed slower than those with shorter wavelengths. The extracted lifetimes ranged from approximately 39 fs to 136 fs for probe wavelengths between 475 nm and 650 nm, consistent with carrier-carrier scattering in graphene, as reported in recent literature.¹⁶



Figure 4.5. (top) Transient Change in Transmission of One, Two and Three-Pass Printed Graphene on Quartz, Following Excitation at 400 nm, from 40 fs to 1200 fs (data cropped to ~800fs), at Room Temperature, (bottom) Kinetic Analysis of All Graphene Samples.

The overall charge dynamics in the three graphene samples were similar, suggesting that sample thickness has a minimal influence. However, the initial positive signal was slightly stronger in thicker graphene samples (II and III), potentially indicating a correlation between thickness and the excitation process. The observed phenomena suggest that the initial positive signal is likely due to the rapid excitation of electrons in the graphene lattice, followed by a carrier-carrier scattering relaxation process. The dependence of the initial positive signal and lifetimes on probe wavelength highlights the importance of energy-dependent processes in graphene's ultrafast dynamics. While sample thickness has a limited influence on the overall charge dynamics, the slightly stronger initial positive signal in thicker samples warrants further investigation to understand the underlying mechanisms.

Sample	GI		GI	l	G III	
Wavelength λ (nm)	Decay Lifetime τ (fs)	Decay ifetime τ (fs) ±τ error		±τ error	Decay Lifetime τ (fs)	±τ error
475	39	±1	53	±5	56	<u>±</u> 4
500	66	±5	83	±5	74	±3
525	95	±7	93	±4	96	±3
550	108	±3	118	±3	113	±3
575	115	±3	120	±3	123	±2
600	120	±4	125	±4	126	±3
625	128	±3	133	±2	130	±3
650	134	±6	135	±3	136	±6

Table 4.2 Lifetimes of Graphene samples (from 40 fs to 1200 fs)

Figure 4.6 focuses on the decay kinetics of the transient change in transmission ($\Delta T/T$) for G I after excitation with a 400 nm laser pulse. The graph illustrates a clear relationship between the decay rate

and the probe wavelength. It shows that shorter probe wavelengths, which have higher maximum $\Delta T/T$ values, exhibit faster decay, while longer wavelengths, with lower maximum $\Delta T/T$ values, decay more slowly. This behaviour is consistent with findings in related studies where shorter wavelengths promote more rapid carrier relaxation through electron-electron scattering due to their higher energy. In contrast, longer wavelengths result in slower decay, likely due to a dominance of phonon-related processes that govern relaxation dynamics at lower energies. This suggests that relaxation rates in graphene are energy dependent: with higher-energy states relaxing faster through electronic interactions, and lower-energy states being more prone to relaxation via phonon coupling. The probe itself only measures the relaxation dynamics, without inducing any noticeable relaxation processes.



Figure 4.6. Transient Change in Transmission Kinetics of One-Pass Printed Graphene on Quartz, Following Excitation at 400 nm.

The optoelectronic response of graphene upon excitation with 400 nm light

Following exposure to 400 nm light, the graphene lattice creates an out-of-equilibrium distribution of photogenerated carriers, specifically electrons (e⁻) and holes (h⁺). This excitation results in photogenerated electrons positioned above the Dirac point and holes below it, separated by the absorbed energy of the excitation photon (E = hc/ λ _pump).¹⁷ This effect, consistently observed across all graphene samples tested, leads to a positive change in transmission (Δ T/T) throughout the spectral range, indicating enhanced transparency of the graphene when exposed to 400 nm light.

Immediately after excitation, bleaching occurs at probe photon energies lower than the pump photon, a phenomenon observed in the literature in similar graphene samples.¹⁸ This effect aligns with reports of bleaching in both non-degenerate and degenerate pump-probe experiments, where probe light at lower energies than the pump shows reduced absorption. These observations suggest that the photogenerated carriers contribute to this bleaching effect, with carrier relaxation dynamics being influenced by the energy and symmetry of the excited states relative to the Dirac point.^{14,18,19,20}

The consistent placement of electrons and holes relative to the Dirac point implies a symmetrical distribution of excited states. However, studies on similar systems suggest that the exact energy levels of these states would depend on factors like the photon energy and the intrinsic properties of the graphene.¹⁷

The transient $\Delta T/T$ signal decays with lifetimes ranging from approximately 40 fs to 140 fs, which are attributed to the cooling of carriers via interactions between the excited carriers and optical phonons within the graphene lattice. These time constants align with those reported for graphene films on quartz substrates, supporting that carrier-phonon interactions play a central role in this decay process.

A comparison of decay lifetimes across different probe wavelengths reveals an important distinction. In the 2009 study by Dawlaty et al.,²⁰ a linear correlation between decay lifetime and probe wavelength was observed across 450 nm to 600 nm. However, the current study has identified a significant deviation from linearity for probe wavelengths below 500 nm. This deviation could be attributed to the different pump wavelengths used in the experiments, 400 nm in the present study compared to 350 nm in the previously published research. The difference in excitation energy likely influences the relaxation pathways of the excited carriers, leading to the observed variation in decay behaviour for shorter probe wavelengths.²⁰

When the probe wavelength approached the pump wavelength, larger coherent artefact signals arose due to the quartz substrate. These artefacts complicated the fitting of kinetic data, potentially leading to less reliable extracted lifetimes. This is evident from the increased error associated with the lifetimes measured in this study.

The literature has previously documented the emergence of a negative $\Delta T/T$ signal during later stages of excitation.²⁰ This behaviour has been linked to two potential factors, which include the doping levels and thermal effects. The presence of dopants within the graphene layers can influence its electronic properties and contribute to the observed negative $\Delta T/T$ signal. Additionally, the excitation process can induce thermal heating of the graphene, potentially altering its band gap and affecting light transmission. Previous studies have reported time constants for the decay of the negative $\Delta T/T$ signal of up to 60 ps.²¹ However, in the current study, attempts to acquire reliable decay data for the negative $\Delta T/T$ signal were disadvantaged by increased noise levels during the experiments. To overcome this limitation and thoroughly explore longer-term dynamics, further experiments with an improved signal-to-noise (S/N) ratio with an extended time window were carried out.



Extended Time Window

Figure 4.7. Kinetics Traces at 475 nm (black), 525 nm (red) and 575 nm (blue) for Graphene I, II and III Following Excitation at 400 nm. The solid traces overlaid are analytic fits using a sum of three exponential decays convolved with a Gaussian function.

The initial investigations using shorter time windows suggested a monoexponential decay for the remaining negative $\Delta T/T$ signal. However, further investigations employing extended time windows

revealed more complex decay characteristics for the remaining negative signal as shown in Figure 4.7. These graphs demonstrate that the negative signal, in fact, exhibits triexponential decay behaviour.

As shown in Figure 4.7, kinetic traces were measured at 475 nm, 525 nm, and 575 nm for G I, G II, and G III. Analytical fits were then applied to these traces to capture the observed behaviour. Table 4.3 summarises the extracted lifetimes (τ 1, τ 2, and τ 3) and their associated errors for each sample at the three wavelengths; the corresponding lifetimes are also depicted in Figure 4.8.



Figure 4.8. Plots of the Lifetimes of the 'Fast' and 'Slow' Decays of Graphene I, II and III Against Probe Photon Wavelength. Associated errors are shown as error bars.

The ultrafast component (τ 1) has lifetimes ranging from approximately 0.06 to 0.1 ps as shown in Table 4.3. Given the extremely short duration of this component, its precise determination might be constrained by the resolution of the experimental instruments. This ultrafast timescale is consistent with mechanisms such as electron-phonon coupling, where electrons interact with lattice vibrations in the material. This coupling could facilitate the rapid dissipation of energy immediately after excitation. Additionally, this ultrafast component may be associated with the swift relaxation of hot carriers following excitation by 400 nm light. Upon light absorption, electrons in the graphene are promoted to higher energy states. The observed ultrafast decay could reflect these hot carriers' initial scattering or relaxation as they interact with phonons, leading to a rapid redistribution of energy within the graphene lattice.²²

			fitting	at 475 nm		
sample	τ1 (ps)	±τ1 error	τ2 (ps)	\pm τ2 error	τ3 (ps)	±τ3 error
GI	0.061	0.004	2.406	0.330	61.573	11.134
G II	0.053	0.005	2.869	0.397	50.466	9.459
G III	0.079	0.003	2.739	0.321	54.904	7.726
			fitting	at 525 nm		
	τ1 (ps)	±τ1 error	τ2 (ps)	$\pm \tau 2 error$	τ3 (ps)	±τ3 error
GI	0.102	0.002	4.355	0.622	73.627	18.262
G II	0.106	0.004	4.160	1.059	36.326	17.715
G III	0.100	0.002	5.289	0.888	60.953	21.803
			fitting	at 575 nm		
	τ1 (ps)	±τ1 error	τ2 (ps)	\pm τ2 error	τ3 (ps)	±τ3 error
GI	0.122	0.004	6.299	1.669	15.576	4.553
G II	0.126	0.003	3.596	1.352	31.736	8.868
G III	0.123	0.002	6.440	1.562	40.565	19.368

Table 4.3 Lifetimes extracted from triexponential fits of ΔT/T Spectra at 475 nm, 525 nm, and 575 nm for graphene samples.

The fast component (τ_2) exhibits a dependence on probe photon wavelength similar to the trend seen in the decay of the initial positive $\Delta T/T$ signal. As detailed in Table 4.3, a consistent increase in τ_2 lifetimes was observed for all three graphene samples as the probe wavelength increased from 475 nm to 575 nm. The extracted lifetimes ranged from 2.4 to 6.4 ps, with graphene sample G I showing the longest lifetimes at each wavelength. One possible explanation for this behaviour is intraband relaxation, where excited electrons relax within the same energy band. The wavelength dependence of τ_2 could be related to the specific energy transitions probed by the incident light. Another possible mechanism is carrier trapping and de-trapping, where electrons are temporarily trapped in localised states and released. However, it's important to note that the error margins suggest that the lifetimes for each wavelength might be statistically equivalent. Trapping typically results in longer-lived states than those observed here, making this a less likely explanation for the τ_2 lifetimes. In comparison, longer-lived trap states have been observed in graphene oxide (GO). Kaniyankandy et al. reported multiexponential decay dynamics in GO with lifetimes ranging from 0.8 ps to over 400 ps, primarily due to electron trapping in oxygen-related defects. This suggests that while fast relaxation processes may influence τ_2 lifetimes here, trapping effects could still play a role, especially at longer timescales, similar to those observed in graphene oxide studies.²³

As indicated in Table 4.3, the slow component (τ 3) did not show a clear correlation with the probe photon wavelength, as shown in Figure 4.8. Each component's contribution to the overall decay profile is likely to vary depending on the specific wavelength and sample. However, the data still suggest the presence of a dominant fast component. The slow component, with lifetimes ranging from 36 to 74 ps, appears to be independent of the probe wavelength, indicating a relaxation process that is not directly linked to the electronic band structure but most likely related to the material's structure, such as defects. Since pure graphene is not expected to exhibit resistance or trapped states, these longer lifetimes may arise from imperfections or oxygen-related trap states in the material.

The extended time window analysis shows a more intricate decay pattern for the negative $\Delta T/T$ signal compared to the original findings. The presence of three distinct decay components with varying

dependence on the probe photon wavelength suggests a complex relaxation process within the graphene samples.

Power Dependence Study

This study investigated the behaviour of kinetic traces under varying excitation powers. The analysis showed a consistent increase in both ultrafast (sub-200 fs) and fast recovery (τ 2) lifetimes across all samples (G I, G II, G III) as the excitation power rose from 0.1 mW to 1.8 mW. However, the trend for the longest lifetime was not as clear.

Fitting the early-time dynamics, particularly around the turning point, for samples G I and G II became more challenging at higher powers (1.4 mW and 1.8 mW). A triexponential function was insufficient for accurately modelling the data at these power levels. The coherent artefact significantly impacted the instrument response function (IRF) for sample G I, especially at shorter wavelengths and higher powers. Masking data points at early times was necessary to minimise this impact on fitting. Analysis of errors and residuals indicated that wavelengths 540 nm and 560 nm provided the most reliable data for G I (Figure 4.9, left) and G II (Figure 4.9, right) when studying sub-200 fs and fast recovery lifetimes. The lifetimes of GI and GII are given in Table 4.4 and Table 4.5, respectively.

Despite encountering challenges in fitting at high powers, the tail fits of the data provided reasonable estimates of the recovery dynamics' lifetimes, indicating that the observed trends are reliable. Further investigation using methods that enable global fitting analysis or deconvolution techniques will be essential to enhance the modelling of the intricate kinetic traces observed at high powers (1.4 mW and 1.8 mW) for all samples.



Figure 4.9. (left) Power Dependence Kinetic Fitting at 540 nm for the G I Sample, and (right) Power Dependence Kinetic Fitting at 560 nm for the G II Sample.

Power		GI fitting	GI fitting at 540 nm				
(μ)	(mW)	τ1 (ps)	± T1 error	τ2 (ps)	± τ2 error	τ3 (ps)	± T3 error
0.02	0.1	0.056	0.009	1.102	0.270	68.619	21.849
0.1	0.5	0.063	0.004	2.751	0.302	53.051	12.291
0.18	0.9	0.080	0.003	3.446	0.606	36.697	13.251
0.28	1.4	0.101	0.003	6.953	1.963	99.226	47.212
0.36	1.8	0.121	0.004	7.449	5.182	69.248	44.835

Table 4.4 Tabulated data for the power dependence kinetic fitting at 540 nm for G I

Power	_	GII fitting	GII fitting at 560 nm					
(щ)	(mW)	τ1 (ps)	± T1 error	τ2 (ps)	± T2 error	τ3 (ps)	± T3 error	
0.02	0.1	0.064	0.006	2.662	0.272	n/a	n/a	
0.1	0.5	0.085	0.010	2.569	0.281	186.685	221.501	
0.18	0.9	0.061	0.004	3.571	0.350	63.693	14.907	
0.28	1.4	0.078	0.004	4.228	1.230	59.899	27.286	
0.36	1.8	0.070	0.001	6.209	1.726	80.370	23.520	

Table 4.5 Tabulated data for the power dependence kinetic fitting at 560 nm for G II sample.

Figure 4.10 illustrates the decay of the transient change in transmission ($\Delta T/T$) for G III film sample at different probe wavelengths and laser powers. The decay curves are analysed using multiple exponential functions, specifically a sum of three or four exponentials, to determine the decay time constants (τ (ps)) as shown in Table 4.6.



Figure 4.10. Power-Dependent Lifetime Analysis of Graphene III Film at Different Wavelengths

Observations from the data in Table 4.6 reveal distinct patterns in the decay time constants ($\tau 1$, $\tau 2$, $\tau 3$, and $\tau 4$) for graphene under varied laser powers and probe wavelengths. Regardless of laser power, $\tau 2$ tends to rise with increasing probe wavelength, implying a delayed relaxation process in graphene for lower-energy probe light. This implies that lower energy photons may infiltrate deeper into the electronic band structure, resulting in more prolonged relaxation pathways.

				G III				
				0.1mW	(0.02 μJ)			
wavelength (nm)	τ1 (ps)	err	τ2 (ps)	err	τ3 (ps)	err	τ4 (ps)	err
525	0.043	0.013	1.090	0.338	64.976	24.485	0.000	
550	0.051	0.007	1.885	0.279	41.691	15.437	0.000	
575	0.048	0.005	0.973	0.189	7.391	1.359	0.000	
				0 5 nm\/	/ (0 101)			
wavelength				0.5 11114	(0.10 µ3)			
(nm)	τ1 (ps)	err	τ2 (ps)	err	τ3 (ps)	err	τ4 (ps)	err
500	0.107	0.009	1.897	0.488	30.020	11.951	n/a	
525	0.099	0.005	2.185	0.468	30.495	10.16	n/a	
550	0.100	0.002	2.089	0.369	16.511	3.457	n/a	
575	0.103	0.002	2.615	0.264	24.817	4.375	n/a	
				0.0	(0.19)			
wavelength				0.9 MW	(0.18 m)			
(nm)	τ1 (ps)	err	τ2 (ps)	err	τ3 (ps)	err	τ4 (ps)	err
500	0.081	0.006	3.337	1.044	61.209	24.306	n/a	
525	0.105	0.004	5.219	1.457	83.965	57.609	n/a	
550	0.114	0.003	6.093	1.758	66.202	42.081	n/a	
575	0.081	0.006	3.337	1.044	61.209	24.306	n/a	
				1.4 mW	(0.281)			
wavelength				1.4 11100	(0.20 µJ)			
(nm)	τ1 (ps)	err	τ2 (ps)	err	τ3 (ps)	err	τ4 (ps)	err
500	0.097	0.009	8.745	4.241	233.585	786.870	n/a	
525	0.101	0.008	0.767	0.751	5.688	3.603	77.640	59.708
550	0.125	0.003	2.282	54.936	2.204	39.941	45.672	12.710
575	0.131	0.005	1.456	2.049	41.946	28.707	3.683	5.717
				1 9 m\\/	(0.201)			
wavelongth				T'9 IIIM	(0.50 m)			
(nm)	τ1 (ps)	err	τ2 (ps)	err	τ3 (ps)	err	τ4 (ps)	err
500	0.085	0.008	0.366	0.216	5.042	2.625	63.698	23.77
525	0.131	0.005	1.627	2.976	3.966	6.916	66.106	43.5
550	0.138	0.004	1.734	4.471	2.431	7.077	52.310	22.715
575	0.137	0.003	0.889	0.255	4.111	2.414	47.799	16.889

Table 4.6 Tabulated data of the impact of excitation power on relaxation processes in Graphene III Film

The impact of laser power on decay times demonstrates diverse patterns depending on the wavelength. At shorter wavelengths, particularly around 500 nm and 525 nm, decay times such as $\tau 1$ generally increase with increasing laser power, indicating faster relaxation. For example, at 525 nm, $\tau 1$ increases from 0.043 ps at 0.1 mW to 0.099 ps at 0.5 mW and then stabilises around 0.105-0.131 ps as power increases further. However, the trend is less consistent at longer wavelengths such as 625 nm and 675 nm. At these longer wavelengths, decay times either remain constant or exhibit a slight increase with laser power.

It is likely that higher laser power results in the excitation of a greater number of electrons in graphene. The decay time constants reflect these excited states' relaxation pathways. The multiple exponential fits suggest the presence of multiple relaxation processes in graphene. The relative contributions of these processes may vary depending on the probe wavelength and laser power. The relaxation mechanisms in graphene could inherently rely on the probe photon energy, which is related to the wavelength. Lower energy photons might have the ability to probe deeper into the electronic band structure, resulting in slower relaxation.

The power dependence studies of $\tau 1$ for all three graphene samples are illustrated in Figure 4.11. A reasonable trend for all the samples, as discussed before, indicates that as wavelength increases, the lifetime also increases. The power dependence study for G I exhibits a steeper slope compared to the other two graphs, suggesting that the lifetime is more sensitive to changes in power in this study. G II and G III also show positive trends. Still, their slopes are shallower compared to G I. This suggests that the lifetimes in G II and G III increase with power but at a slower rate than G I. The large error bars for G III indicate that the data points in that plot might be less reliable.



Figure 4.11. Lifetime vs Beam Power (Fluence) Plots of GI, GII, GIII.

Aerogel Graphene (AG) I, II and III

Aerogel graphene (AG) samples with different thicknesses (AG I, II and III) were subjected to the same analysis. The measurements were conducted at room temperature. In Figure 4.12, the top panel illustrates the transient change in transmittance ($\Delta T/T$) over time following a 400 nm light pulse. This time evolution occurs within a remarkably short timeframe, ranging from 20-40 femtoseconds (fs) to a slightly longer window of 1080-1200 fs. However, due to technical limitations, it is not possible to reliably monitor processes that occur under 100 fs. To obtain a deeper understanding of the observed dynamics, the bottom panel of Figure 4.12, presents a kinetic analysis for all AG samples. Complementing the information in Figure 4.12, Table 4.7 provides the decay lifetimes extracted from the transient transmission measurements. The table focuses on three specific AG samples and analyses their behaviour at different wavelengths of light. The decay lifetime τ_2 was consistently found to be non-decaying (∞) for all samples and wavelengths investigated.

Sample		AG I			AG II			AG III	
	Decay		Decay	Decay		Decay	Decay		Decay
Wavelength	Lifetimes		Lifetimes	Lifetimes		Lifetimes	Lifetimes		Lifetimes
λ (nm)	τ1 (fs)	errors	τ2 (fs)	τ (fs)	errors	τ2 (fs)	τ (fs)	errors	τ2 (fs)
475	58	±5	∞	89	±2	∞	88	±3	∞
525	87	±4	∞	113	±2	∞	110	±3	~
575	99	±6	∞	135	±2	∞	121	±2	~
625	94	±3	∞	147	±3	∞	124	±2	∞

Table 4.7 Lifetimes of initial AG experiments from 20-40 fs to 1080-1200 fs

Note: 'Infinite' indicates non-decaying within the experimental time window



Figure 4.12. (top) Transient Change in Transmission of One-Pass Printed Aerogel Graphene on Quartz, Following Excitation at 400 nm, from 20-40 fs to 1080-1200 fs, at Room Temperature, (bottom) Kinetic Analysis of all AG Samples.

All AG samples displayed a positive $\Delta T/T$ signal across the measured spectral range (430 nm to 680 nm) upon excitation with a 400 nm light pulse. This initial transmittance increase likely originates from the excitation of electrons within the AG. The observed positive $\Delta T/T$ signal decayed bi-exponentially across the entire spectral range, indicating two main processes governing the relaxation of excited electrons back to their ground state. The decay lifetimes of the $\Delta T/T$ signal varied with the probe wavelength, with longer wavelengths resulting in a slower decay rate compared to shorter ones. Table 4.7 provides the two decay lifetimes (τ_1 and τ_2) for each sample-wavelength combination, offering a more detailed description of the relaxation dynamics for the short time window of these experiments. The initial increase in transmittance ($\Delta T/T$) and the fast decay process (τ_1) likely reflect carrier–carrier scattering and electron-phonon scattering, where the excited electron loses energy by interacting with the vibrations of the graphene lattice.^{17,20} This process may be faster at shorter wavelengths because higher energy electrons typically scatter more readily. The three-dimensional structure of the aerogel graphene may introduce a more intricate pathway for electron relaxation compared to flatter twodimensional graphene films, potentially contributing to the observed bi-exponential decay. Additionally, the presence of small amounts of oxygen within the AG can introduce defect states that serve as traps for excited electrons. The second, non-decaying component ($\tau_2 = \infty$) could be attributed to electrons getting trapped in defect states introduced by oxygen within the AG. These traps can create deep energy levels, potentially leading to a much slower relaxation process that might not be captured within the timeframe of this experiment.

Longer Time Window Experiments

Building upon the investigations presented in Figure 4.12, Figure 4.13 explores the photoexcitation dynamics of aerogel graphene samples at a longer time window of 400 ps, to investigate the non-decaying component further. The excitation source remains a 400 nm light pulse, and the analysis focuses on a wavelength range of 500 nm to 600 nm.



Figure 4.13. Kinetics Traces at Wavelengths Ranging from 500 nm to 600 nm for AG I, II and III Following Excitations at 400 nm. The solid traces overlaid are analytic fits using a sum of three or four exponential decays convolved with a Gaussian function.

				AG I			
Wavelength λ (nm)	τ1 (ps)	errors	τ2 (ps)	errors	τ3 (ps)	errors	τ4 (ps)
520	0.016	0.010	0.164	0.016	0.002	4.814	∞
560	0.125	0.004	0.621	0.199	8.242	16.148	∞
600	0.138	0.003	0.919	0.339	11.591	15.892	∞
				AG II			
Wavelength λ (nm)	τ1 (ps)	errors	τ2 (ps)	errors	τ3 (ps)	errors	τ4 (ps)
520	0.126	0.002	1.777	0.672	21.944	8.274	∞
560	0.140	0.002	2.324	1.713	24.668	17.603	∞
600	0.138	0.002	2.528	2.625	30.097	30.897	∞
				AG III			
Wavelength λ (nm)	τ1 (ps)	errors	τ2 (ps)	errors	τ3 (ps)	errors	τ4 (ps)
520	0.132	0.003	1.700	0.931	29.712	13.199	∞
560	0.127	0.002	0.753	0.138	36.259	11.626	∞
600	0.143	0.001	1.215	0.257	34.995	11.474	∞

Table 4.8 Extracted decay timescales from AG photoexcitation kinetics (λ = 500-600 nm, 400 ps)

The solid lines overlaid on Figure 4.13 depict analytic fits to the measured kinetics traces. These fits involve a combination of three or four exponential decays to capture the complex relaxation behaviour observed, indicating the contribution of multiple relaxation processes to the overall decay of the excited state population. The timescales associated with these pathways vary, with some

relaxation processes occurring on ultrafast timescales (tens of femtoseconds) and others on picosecond timescales. Carrier–phonon scattering, phonon–phonon scattering, electron-hole recombination, and potential trapping at defect states induced by the presence of oxygen could all contribute to the observed behaviour.²⁴ Table 4.8 and Table 4.9 provide a summary of the extracted decay lifetimes (τ) for each AG sample and wavelength combination. Table 4.8 displays the initial fit results, while Table 4.9 demonstrates the refined fit for AG I due to the excessively large errors in the initial attempt.

AG I (fitted again)								
Wavelength λ (nm)	τ1 (ps)	errors	τ2 (ps)	errors	τ3 (ps)			
520	0.108	0.011	0.511	0.011	∞			
560	0.129	0.006	0.786	0.006	8			
600	0.136	0.003	0.632	0.131	8			

Table 4.9 Repeated and revised deca	y timescales for AG I photoexcitation	n kinetics (λ = 500-600 nm, 400 ps)
-------------------------------------	---------------------------------------	-------------------------------------

As seen in Table 4.8 and Table 4.9, the decay lifetimes (τ) are derived from fitting the measured data with exponential decay functions. These lifetimes characterise the timescales for various relaxation processes occurring within the aerogel graphene samples. The analysis reveals a range of timescales, from ultrafast (fs) to picoseconds. The rapid decay (τ_1) is likely a result of carrier-phonon scattering, in which excited electrons dissipate energy through interactions with the vibrations of the graphene lattice, consistent with the findings in Huang et al.'s study.²⁴ The slower decay components may be linked to processes such as phonon-phonon scattering, lattice vibration interactions, or electron-hole recombination. It is worth noting that all samples show a non-decaying component (τ_4), indicating a long-lasting population of excited electrons persisting beyond the 400 ps timeframe of the experiment, possibly due to electron trapping at defect states introduced by oxygen within the aerogel structure.

Comparison of Graphene and Aerogel Samples

Initial Lifetimes



Figure 4.14. Comparing the Initial Decay Lifetimes of G vs AG After Photoexcitation Dynamics Across Wavelengths Taken from the Short Time Window Experiments.

The decay lifetimes of excited states vary noticeably but non-systematically between AG and G samples at different wavelengths (Figure 4.14), suggesting distinct relaxation behaviours for excited electrons in these materials. The distinctive structural characteristics of aerogel and graphene can influence the relaxation pathways for excited electrons. The 3D porous-like structure of aerogel may lead to more intricate relaxation mechanisms compared to the flatter, layered structure of graphene. Furthermore, the presence of defects or dopants, such as oxygen groups, within the materials could create traps for excited electrons, potentially extending the lifetime of the excited state and impacting

the observed decay times. Overall, the pure graphene film samples show a stronger positive correlation between their initial decay lifetimes and the wavelengths, although the trend is also noticed for the AG films.

Power dependence comparison of AG III and G III

In Figure 4.15, Table 4.10 and Table 4.11, the power dependence of samples G III and AG III is compared. The study involved excitation at a 400 nm laser pulse with a wavelength of 550 nm. The data is presented as a plot of $\Delta T/T$ vs. time delay, where ΔT represents the change in transmission and T is the initial absorbance. G III at lower Ep was fitted using a bi-exponential function; at powers of 0.5 mW and 0.9 mW, it was fitted predominantly using triexponential functions.



Time delay / ps

Figure 4.15. Power Dependence of Excited State Lifetimes in G III and AG III

Pump energy (<i>E</i> _p)	G III fitting at 550 nm							
(mW)	τ1 (ps)	$\pm \tau 1 \text{ error}$	τ2 (ps)	$\pm \tau 2 \text{ error}$	τ3 (ps)	± τ3 error	τ4 (ps)	± τ4 error
0.2	0.047	0.007	2.67	0.264	n/a	n/a		
0.5	0.1	0.002	2.089	0.369	16.511	3.457	n/a	
0.9	0.114	0.003	6.093	1.758	66.202	42.081	n/a	
1.4	0.125	0.003	2.204	39.936	2.282	54.928	45.672	12.709
1.8	0.138	0.004	1.734	4.471	2.431	7.077	52.31	22.715

Table 4.10 Tabulated data for the power dependence kinetic fitting at 550 nm for G III sample.

Table 4.11 Tabulated data for the power dependence kinetic fitting at 550 nm for AG III sample.

Pump energy (<i>E</i> _p)	AG III fitting at 550 nm							
(mW)	τ1 (ps)	± τ1 error	τ2 (ps)	$\pm \tau 2 \text{ error}$	τ3 (ps)	±τ3 error	τ4 (ps)	± τ4 error
0.2	0.092	0.002	2.67	0.264	39.32	13.528	n/a	
0.5	0.117	0.002	0.523	0.092	60.679	13.114	~	0
0.9	0.143	0.002	0.78	0.171	42.445	11.982	∞	0
1.4	0.129	0.003	0.572	0.089	50.744	12.851	~	0
1.8	0.144	0.003	0.648	0.091	59.283	11.286	∞	0

At higher power, G III was fitted using four exponential functions. This signal dependence implies that the nature of the initial carrier relaxation mechanism changes as Ep increases. This behaviour may be due to a hot optical phonon bottleneck at higher pump energies. After being excited, the hot carriers can lose most of their energy by forming hot optical phonons through successive carrier optical phonon scattering events. On the other hand, AG III was primarily fitted using a four-exponential fit function (except for the lowest Ep (0.2 mW), where AG III was fitted using a tri-exponential fitting function) exhibiting a non-decaying lifetime at beam powers equal to or greater than 0.5 mW. The pump-probe time delay at which the maximum negative signal is reached in AG3 is independent of Ep. It was observed that G III displays a faster-excited state relaxation compared to AG III, particularly at higher excitation powers.

AG III is expected to have more defects and oxygen vacancies, likely creating trapped states that could affect the relaxation dynamics. The number of layers in AG was not expected to influence these dynamics significantly. Furthermore, the excitation energy was expected to play a crucial role in determining the relaxation pathways in these graphene-based samples.

Summary and Discussion of Pump-Probe Results

In summary, the pump-probe measurements revealed distinct relaxation dynamics for both graphene and aerogel graphene samples upon photoexcitation. Graphene films exhibited a predominantly mono-exponential decay at shorter time scales, which aligns with carrier-carrier scattering and electron-phonon interactions. In contrast, aerogel graphene consistently displayed a bi-exponential decay, indicating more complex relaxation pathways likely influenced by its 3D porous structure and the presence of oxygen-related defects.

The studies on power dependence indicated that the relaxation dynamics of both materials are affected by the excitation power. In graphene, higher power levels resulted in increased decay times, potentially due to the formation of a hot electron-phonon distribution. On the other hand, in aerogel graphene, higher power often led to the emergence of longer-lived components, likely related to electron trapping at defect sites. The observed differences in relaxation dynamics underscore the significant impact of material structure and defect density on the behaviour of excited states in these materials.

4.1.4. Discussion

The properties, such as the photo-induced carrier dynamics of graphene (G) compared to silver (AG) injection films, were investigated using ultrafast transient absorption spectroscopy. Ultrafast spectroscopy is well-suited for examining the photoinduced carrier dynamics relevant to graphene's performance. These studies are crucial for sensor applications and for understanding the carrier dynamics that impact the performance of ultrafast electronic devices, such as carrier-carrier or phonon scattering. Furthermore, charge transfer is influenced by the transient conductivity of hot carriers above the Fermi level in certain devices, such as gas sensors. Graphene-based gas sensors work by detecting changes in electrical resistance when gas molecules interact with the graphene surface, leading to charge transfer that alters its conductivity.^{25,26}

The AG samples are expected to contain a higher oxygen content compared to G, due to the synthesis procedure, leading to the development of a more intricate 3D structure in the films, as revealed by SEM images. No XPS data for AG is presented in this section, but a comparison between XPS data of AG and G will be made in the subsequent sections. Similarities in the transient absorption spectra in the 55-140 fs range suggested a similar lattice defect density in both AG and G. While G demonstrated a complete recovery of the transient signal, AG exhibited only partial recovery in the 400 picoseconds experiment, indicating the possible presence of trapped electronic states, likely attributed to the oxygen content.

The $\Delta T/T$ spectra obtained from exciting the graphene samples at 400 nm exhibit similarities among all three samples. The signal initially shows a positive $\Delta T/T$ trend, followed by decreases, resulting in

negative $\Delta T/T$ signals. The lifetime of the signal depends on the probe wavelength, with thicker samples and longer wavelengths yielding a more pronounced initial positive signal.

It is well-established in current scientific understanding that graphene exhibits various decay components, namely ultrafast, fast, and slow, and their potential origins in the electronic structure. Specific relaxation mechanisms, such as electron-phonon coupling for ultrafast decay, are tentatively assigned to the observed decay components, based on established scientific knowledge. However, it's worth noting that these are potential mechanisms, and further experimental or theoretical work may be needed for definitive identification. The ultrafast timescale of the first component poses a challenge for definitive resolution due to instrumental limitations.^{16,19}

Both G and AG films exhibited similar timescales, with carrier-optical phonon (C-OP) scattering occurring within 74-136 fs for G and 110-126 fs for AG. This similarity suggests that the density of defects in the crystal lattice, which can scatter hot carriers, is comparable between the two types of films. Moreover, the rate of C-OP scattering increased with the energy of the probe light used in the experiment, indicating that carriers with higher initial energy lose their energy faster through interactions with lattice vibrations. Upon excitation with a laser pulse, both films demonstrated a positive change in transmission ($\Delta T/T$) signal. This is attributed to the excited electrons blocking transitions from the valence to the conduction band, resulting in reduced overall light absorption. However, the recovery of this signal varied between the films. The negative $\Delta T/T$ signal decayed in two stages ($\tau 1 = 6.1$ ps and $\tau 2 = 64$ ps), which were attributed to carrier recombination and subsequent lattice cooling. The recovery was slower, and an additional time constant was needed to describe the initial growth of the negative signal, indicating a new process occurring in AG films.

As discussed in this section, the presence of oxygen in Aerogel Graphene inks introduces a critical distinction in carrier dynamics compared to pure graphene samples. The incorporation of oxygen creates trap states within the electronic structure of AG films. These trap states function as energy wells, capturing electrons excited by laser pulses. Electrons trapped within these states struggle to recombine with holes, resulting in a significantly slower recovery of the negative $\Delta T/T$ signal observed. The persistent signal at later time delays (>400 ps) is associated with the slow recombination of electrons trapped in the oxygen-induced states.¹⁹ The 3D structure of AG films may be influenced by their oxygen content, which could also account for the observed differences. Further research is needed to fully understand the impact of oxygen.

The substrate is expected to have minimal to no effect on relaxation dynamics, as the data is chirpcorrected and coherent artifacts are removed, effectively eliminating any influence from the quartz substrate. Transient absorption data is consistently chirp-corrected to ensure accuracy, and the details of the chirp correction procedure are provided in the Appendix. However, it is important to consider that the refractive index of the substrate can still play a role in transient absorption spectroscopy (TAS) measurements. As discussed by Pasanen et al, variations in the refractive index at the film-substrate interface can influence reflectance and transmittance, potentially affecting the measured TAS signals.²⁷ These effects are particularly relevant for thin films, where the optical path length is comparable to the wavelength of light, leading to differences in TAS results between thin films and bulk materials.

The next section will delve into the analysis of films with different oxygen contents to gain deeper insights into the role of oxygen. Moreover, the current study only explored pump energies up to 0.38 μ J. At higher excitation levels, phenomena like hot phonon bottlenecks could lead to further discrepancies in the behaviour of AG films compared to G.

4.2. SAMPLE SET 2: AEROGEL GRAPHENE FILMS WITH VARYING OXYGEN CONTENT PRINTED ON KAPTON TAPE SUBSTRATE

4.2.1. Sample Description

Batch two consisted of 42 film samples, of which three were diluted graphene samples with 1, 2 and 3 printed layers (similar to batch 1), along with AG samples with varying oxygen content; all samples were printed via inkjet printing technique, the same as batch 1 samples, on a yellow flexible tape substrate called Kapton. A table describing each sample is given in the appendix, along with a picture of the samples.

The Kapton substrate AG samples had four variations with different oxygen content in the ink named 0.3, 0.4, 0.5, and 0.75. The number indicates the oxygen-to-carbon ratio of the inks before printing and not the concentration of oxygen in the final films. Half of the samples underwent an additional heat treatment process called annealing. Each variant had samples with 1, 2, and 3 printed layers; in addition, there were two versions of each sample, a diluted and an undiluted ink sample. Most of the undiluted films were too thick and dark to perform UV-Vis Steady state and transmission TA on. Therefore, reflectance mode TA was attempted.

4.2.2. Characterisation Methods

4.2.2.3. Pump-Probe Spectroscopy

The experiments for this section largely mirrored section 4.1.2.2, employing the same setup and procedures for UV-Vis pump-probe spectroscopy. However, unlike section 4.1.2.2, which explored the effects of varying pump pulse energy, this section focused on a fixed pump pulse energy and only the sapphire crystal was used for the generation of the white light. Additionally, some measurements in this section employed reflectance mode instead of the transmission mode.⁸

4.2.2.1. FTIR

An analysis using FTIR and ATR was performed at the Chemistry Department of the University of Sheffield using a cutting-edge FTIR spectrometer with an ATR accessory. The instrument operates within a wavenumber range of 400 to 4000 cm⁻¹, delivering a thorough analysis of the sample's infrared absorption spectrum.²⁸

4.2.2.2. XPS

The XPS experiments were carried out at the Sheffield Surface Analysis Centre, like the experiments in section 4.1.2.3. However, instead of surveying the silicon present in SiO2, nitrogen was additionally surveyed in these samples, as the Kapton tape substrate contains nitrogen. The Kapton tape was also analysed using XPS for comparison with the AG film samples.⁵

4.2.2.4. AFM

AFM, with the same setup as in section 4.1.2.5, was used to capture the height profiles of the sample 0.5 AG with 3 printed passes and 0.75 AG with 3 printed passes (both diluted inks).¹¹

4.2.3. Results

4.2.3.1. Transient Absorption Results

Transient Absorption in Transmittance Mode

Transient absorption measurements were carried out for two AG films: AG 0.3 and AG 0.75 with low and high oxygen content, respectively.

Lower Oxygen Content AG Film 0.3 on Kapton Tape

This section investigates the relaxation processes of the AG diluted ink thin film with a low oxygen content of 0.3 deposited on a Kapton tape substrate. The results are presented in Figure 4.16 a, Table

4.12 and Table 4.13. Similar to the previous investigation in section 4.1, the AG film on Kapton initially shows a positive $\Delta T/T$ signal, suggesting increased transmission after excitation and indicating that the material enters an excited state. The signal then decays over time across all measured wavelengths, indicating relaxation back to the ground state. The decay is faster for shorter probe wavelengths (higher energy) and slower for longer wavelengths (lower energy), a behaviour commonly observed in materials where relaxation is influenced by the energy levels involved.



Figure 4.16. Transient Absorption Study of (lowest oxygen content) AG 0.3 Film Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 35 to 670 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.6 to 400 ps (left) and its kinetic analysis at different wavelength (right).

Table 4.16 illustrates the transient change in transmission ($\Delta T/T$) for early and late time window experiments of AG 0.3, as well as the corresponding kinetic analysis at various wavelengths. Table 4.12 Early Time Kinetics of AG 0.3 on Kapton (35-670 fs) presents the kinetic lifetimes extracted from the early time (up to 670 fs) experiments. The lifetimes extracted from fitting the $\Delta T/T$ spectra in the short time window (35-670 fs) show two components: $\tau 1$, an ultrafast lifetime, and $\tau 2$, an infinite lifetime, indicating the presence of non-decaying factors. Table 4.13, on the other hand, displays the lifetimes extracted from fitting the $\Delta T/T$ spectra in the long-time window (0.6 ps - 400 ps), revealing multiple decay components ($\tau 1$ to $\tau 4$) for all wavelengths, again with the non-decaying factor (∞) for some. The presence of these non-decaying factors in the tables suggests the potential existence of long-lived excited state populations or other unresolved decay processes contributing to the signal, which could be due to the electrons trapped in the oxygen-induced states.¹⁹ The presence of multiple decay components in the long time window indicates the involvement of various relaxation pathways. These may include electron-phonon coupling and the interaction between excited electrons and vibrations within the AG film lattice, as well as vibrational relaxation and energy transfer to the Kapton substrate.

AG 0.3 on Kapton early time lifetimes									
Wavelength (nm)	τ1 (fs)	± τ1 error	τ2 (fs)	± T2 error					
450	81.0	4.0	~	0.0					
500	87.0	3.0	~	0.0					
550	105.0	2.0	∞	0.0					
600	119.7	3.0	∞	0.0					
650	123.1	6.5	∞	0.0					

Table 4.12 Early Time Kinetics of AG 0.3 on Kapton (35-670 fs)

Table 4.13 Late Time Kinetics of AG 0.3 on Kapton (0.6 ps - 400 ps)

AG 0.3 on Kapton late time lifetimes								
Wavelength (nm)	τ1 (ps)	± T1 error	τ2 (ps)	± T2 error	τ3 (ps)	± T3 error	τ4 (ps)	± T4 error
450	0.078	0.003	34.771	19.426	~	0.0	n/a	
500	0.083	0.001	12.852	427.855	13.699	527.757	∞	0.0
550	0.100	0.001	2.589	1.288	16.469	12.123	∞	0.0
600	0.112	0.002	1.480	0.441	∞	0.0	n/a	
650	0.109	0.003	0.908	0.337	n/a		n/a	

A Higher Oxygen Content, 0.75 AG, on Kapton Tape

Similar to the investigation of the lower oxygen content AG film (0.3 AG), processes in a thin film of AG with the highest oxygen content (0.75 AG) deposited on a Kapton tape substrate were also investigated. Figure 4.17 shows the transient absorption study of the AG 0.75 film. The top graphs display the transient change in transmission for a short time window after excitation with 400 nm light, along with the corresponding kinetic analysis at different wavelengths. The bottom graphs show the transient change in transmission for a longer time window and the corresponding kinetic analysis at different wavelengths. The bottom graphs show the transient wavelengths. The lifetime data extracted from the $\Delta T/T$ spectra fitting is summarised in Tables 4.14 and 4.15 for the short and long-time windows, respectively. The presence of non-decaying factors (∞) in both tables indicates the potential existence of long-lived excited state populations or unresolved decay processes contributing to the signal, comparable to what was observed for the lower oxygen content AG film. Additionally, the observation of multiple decay components in the long time window of 0.7 ps - 400 ps (Table 4.15) suggests the presence of several relaxation mechanisms with different timescales, as was also seen in the case of lower oxygen content.



Figure 4.17. Transient Absorption Study of AG 0.75 Film with the Highest Oxygen Content Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 45 to 750 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.7 to 400 ps (left) and its kinetic analysis at different wavelength (right).

AG 0.75 on Kapton early time lifetimes								
Wavelength (nm)	τ1 (fs)	± τ1 error	τ2 (fs)	± τ2 error				
500	76.3	2.5	~	0.0				
550	91.0	2.0	~	0.0				
600	103.5	1.8	∞	0.0				
650	111.8	2.6	∞	0.0				

Table 4.14 Early Time Kinetics of AG 0.75 on Kapton (45-750 fs)

Table 4.15 Late Time Kinetics of AG 0.75 on Kapton (0.7 ps - 400 ps)

AG 0.75 on Kapton late time lifetimes									
Wavelength (nm)	τ1 (ps)	$\pm \tau 1 \text{ error}$	τ2 (ps)	$\pm \tau 2 \text{ error}$	τ3 (ps)	$\pm \tau 3 \text{ error}$			
500	0.076	0.004	7.037	2.022	∞	0.000			
550	0.099	0.004	10.777	2.849	\sim	0.000			
600	0.109	0.003	18.807	4.441	\sim	0.000			
650	0.110	0.003	41.591	17.584	~	0.000			
Influence of Oxygen Content on Carrier Decay in AG 0.3 and AG 0.75 on Kapton

Both films show a similar initial rise in $\tau 1$ values, with AG 0.3 consistently having a higher $\tau 1$ compared to AG 0.75 at all measured wavelengths. This indicates faster carrier cooling (shorter lifetime) in the film sample with higher oxygen content (AG 0.75). Both samples exhibit an increase in the faster decay component ($\tau 1$) as the wavelength (λ) increases, indicating a slower decay and a longer lifetime at longer wavelengths. This trend is observed in both AG 0.3 and AG 0.75, but it appears to be more pronounced for AG 0.3.

The number of decay components differs between the films. AG 0.75 shows mostly three components across all wavelengths, while AG 0.3 exhibits three to four components ($\tau 1$ to $\tau 4$) depending on the wavelength. This suggests potentially more complex decay processes in the sample with lower oxygen content. The overall lifetimes for AG 0.75 are generally longer than those of AG 0.3 across most wavelengths, particularly for $\tau 2$ and onwards. This again suggests faster decay processes in the material with lower oxygen content.

In general, both samples show similar trends in how decay times are affected by probe wavelength for the initial, faster component (τ 1). However, the presence and number of additional decay components differ, indicating more intricate relaxation processes in the material with lower oxygen content. Higher oxygen content tends to result in longer decay times across the measured range, suggesting slower carrier cooling and relaxation processes. Further investigation may be necessary to determine the cause of the observed differences in decay times resulting from variations in oxygen content.

The tables of the early and late lifetime of AG 0.4 and AG 0.5 are shown in the Appendix alongside their associated graphs.



Kinetics Lifetimes of all Diluted AG on Kapton Samples

Figure 4.18. Initial Ultrafast Recovery Lifetime vs Wavelength for AG/Kapton Samples

The early lifetimes for AG samples printed on Kapton tape are plotted with their associated error bars in Figure 4.18. The graphs show a consistent increase in the initial ultrafast recovery lifetimes for all diluted AG samples as the wavelength of the excitation light increases. This suggests that during the initial stages of relaxation, it takes longer for the lower energy excited state to return to the ground state.

The data in Figure 4.19 illustrates the combined kinetics of all AG on Kapton samples at 550 nm after being excited with a 400 nm light pulse. The early-time experiments show a positive $\Delta T/T$ signal, indicating the excitation of carriers in the AG sample, leading to increased transmission (bleaching). As for the decay of the positive $\Delta T/T$ signal in the early response, it suggests the relaxation of excited carriers, possibly through phonon scattering. In the late-time experiments, the negative $\Delta T/T$ signal suggests the presence of long-lived processes that affect the material's transmission, potentially related to carrier trapping or possible thermal effects. Since recombination would result in a return to normal transmission, this is unlikely to be the dominant mechanism. Instead, thermal effects such as changes in the material's refractive index could influence the negative $\Delta T/T$ signal, as localised heating or lattice distortions can impact the optical properties.¹⁹



Figure 4.19. Combined Kinetics of Early and Late Lifetimes of AG Printed on Kapton Samples: (left) Early Time Study, (right) Cropped Late Time Study, Both at 550 nm, with the Full Data given in the Inset.

Transient Absorption in Reflectance Mode

In pump-probe spectroscopy, the combination of reflectance (R) and transmittance (T) measurements allows for a comprehensive investigation of a material's reaction to photoexcitation. This approach leverages the exclusive strengths of each technique to provide complementary insights into the dynamics of the excited state. Reflectance primarily probes the material's near-surface region, while transmittance examines the entire sample volume. The two measurements also have different sensitivities to changes induced by the pump pulse. Reflectance reveals the photo response near the surface, while transmittance offers information about the overall response throughout the bulk material. Additionally, interference effects can impact the reflectance signal in materials with specific optical properties and thicknesses. By using the same sample for both types of measurements, the consistency of observed trends can be verified.



Figure 4.20. Kinetics Fittings of Early Time and Late Time Reflectance Experiments Against Transmittance Experiments of Samples AG 0.3 (left) AG 0.4 (right), the Black Lines are all T and the Coloured Lines Represent R.

In Figure 4.20, the results of kinetic fittings from pump-probe spectroscopy experiments conducted on samples AG 0.3 and AG 0.4 are presented. The data compares the reflectance (R), depicted by coloured lines, and the transmittance (T), represented by black lines. The fittings analyse the response at early times, shortly after the pump pulse and late times, after the initial response. R measures the portion of light reflected by the sample, while T measures the fraction of light that passes through it. The observed trends in the R and T data for both samples exhibit a high degree of similarity, specifically in the early time window. The consistency observed between the R and T data implies that both reflection and transmission modes provide complementary and accurate insights into the photoexcitation dynamics occurring within the AG samples, as seen for early-time dynamics. However, in the long-time window graphs, the R results show a positive signal after ~ 90 ps, while the T data show a negative signal throughout.



Figure 4.21. Transient Change in Transmission of Sample AG 0.4 Following Excitation at 400 nm. The graphs on the left side show the trace over time in reflectance mode compared to the graphs on the right side that show transmittance mode ((top) early time experiments (bottom) long time experiments).

In Figure 4.21, the interaction between reflected and transmitted light (R and T) in the diluted film AG 0.4 when stimulated by 400 nm light are depicted. In the early time experiments (top graphs), both the R and T graphs depict a sudden change in their values shortly after the 400 nm excitation pulse. The transmittance (T) graph shows a distinct decrease, indicating reduced light transmission through the sample initially. In contrast, the reflectance (R) graph shows a corresponding increase, signalling an initial increase in light reflection. In the longer time experiments (bottom graphs), the changes in R and T occur over a much longer period compared to the top graphs. The R data window is 0.8 to 250 ps, while the T data ranges from 0.6 to 400 ps. Both the R and T graphs show a gradual decline in their values over time. The transmittance gradually returns to its original value, suggesting increased light transmission as time progresses, despite the longer experimental window. The reflectance also slowly decreases back to its baseline value, indicative of reduced light reflection over time.

Figure 4.22 shows the transient transmittance (right) and reflectance (left) kinetics at 550 nm for early time window experiments of AG 0.3 to AG 0.5 samples. The reflectance graph shows a rapid decrease in reflectance following the pump pulse, which could be due to a number of factors, such as the excitation of electrons from the ground state to an excited state, or a change in the material's surface morphology. The initial trends in both graphs are similar, which is expected because reflectance and transmittance are interconnected. A decrease in reflectance often leads to an increase in transmittance, and vice versa.



Figure 4.22. Kinetic Fitting at 550 nm for the Early time Window Experiments for Samples AG 0.3, 0.4 and 0.5 in Both Reflectance and Transmittance Mode Following Excitation at 400 nm at Room Temperature.

The lifetimes of the reflectance (Δ R/R) and transmittance (Δ T/T) for the late-time window experiments were extracted and presented in Table 4.16. The values show some similarities and some differences in terms of the relaxation processes at 550 nm. Both Δ R/R and Δ T/T data show multiple time constants for all samples. This suggests that the relaxation processes after excitation involve multiple steps with different characteristic timescales in both the surface region probed by reflectance and the bulk probed by transmittance. The first time constant (τ 1) for Δ R/R and Δ T/T is relatively similar across all samples. This might indicate that the initial relaxation process has a comparable timescale at the surface and throughout the sample thickness.

Kinetics Summary Comparison of Reflectance and Transmittance (Late Time) at 550 nm								
Sample	Condition	τ1 (ps)	τ2 (ps)	τ3 (ps)	τ4 (ps)			
	ΔR/R	0.15	0.16	59.94	~			
AG 0.3	ΔΤ/Τ	0.10	2.59	16.47	~			
	ΔR/R	0.14	0.16	49.42	~			
AG 0.4	ΔΤ/Τ	0.12	3.03	2.83	~			
	ΔR/R	0.13	3.13	60.57	~			
AG 0.5	ΔΤ/Τ	0.11	0.47	55.26	0.00			

Table 4.16 Comparison of Reflectance and Transmittance (Late Time) Lifetimes for AG 0.3 to 0.5 samples at 550 nm

The subsequent time constants ($\tau 2$ and $\tau 3$) show more variation, especially for samples AG 0.3 and AG 0.4. This suggests that the later relaxation processes might occur at different rates depending on the probed region (surface vs. bulk) and the sample condition. The $\Delta R/R$ lifetime values are generally shorter compared to $\Delta T/T$ values, indicating faster relaxation at the surface than in the bulk of the sample.

While both $\Delta R/R$ and $\Delta T/T$ data exhibit some similarities, particularly in the early time window, the differences in time constants and the magnitude of changes suggest distinct relaxation dynamics between the bulk and surface regions of the samples in the late time window. The early-time relaxation processes are more similar, as seen in Figure 4.22. However, for long-time dynamics, $\Delta R/R$ exhibits a positive signal after ~90 ps, while $\Delta T/T$ remains negative throughout, indicating differing relaxation behaviour between the surface and bulk regions.

Disclaimer

Dr A. Auty conducted most of the reflectance mode pump-probe spectroscopy experiments in this section.

4.2.3.2. FTIR

Figure 4.23 presents FTIR spectra of Kapton alongside AG samples labelled 0.5 and 0.75. The spectra were acquired for both the annealed and unannealed versions of these films. The prominent peaks within the Kapton tape substrate were identified using Table 4.17.



Figure 4.23. FTIR Spectra of Kapton, AG 0.5 (Annealed and Unannealed), and AG 0.75 (Annealed and Unannealed)

Table 4.17 Table of IR absorption. 29

Functional Group	Frequency (cm-1)	Comments
O-H stretching (free)	3700-3580	Broad peak due to hydrogen bonding.
O-H stretching (bonded)	3200-2700	A narrower peak is seen in carboxylic acids and phenols. Stretching vibrations of C-H bonds in
C-H stretching	2830-2695	alkanes.
C=O stretching (aldehyde)	1740-1720	Characteristics of aldehydes also overlap with esters.
C=O stretching (ketone)	1745-1715	Typical for ketones, slightly different from aldehydes. Found in esters, slightly higher than
C=O stretching (ester)	1750-1720	aldehydes.
C=O stretching (amide)	1690-1630	Lower frequency due to resonance effects in amides.
C=C aromatic	1600-1400	Typical of aromatic rings, multiple bands are present.
CH2 bending	1480-1440	Associated with CH ₂ groups in alkanes.
CH3 bending	1465-1440, 1390-1365	Characteristics of CH₃ groups involve both symmetric and asymmetric bending.
C-O-C stretching	1250-1050	Found in ethers and esters, may show multiple peaks.
C-OH stretching	1200-1020	Seen in alcohols and phenols; may overlap with C-O stretching.
C-O stretching	1124-1087	Specific for alcohols and phenols; overlaps with C-OH stretching.



Figure 4.24. The Chemical Structures of Kapton (1)³⁰, Ethylcellulose (2)³¹, Terpineol (3)³² and Cyclohexanol (4) (drawn using ChemDraw)³³

The chemical structures of Kapton, Ethylcellulose, Terpineol, and Cyclohexanol are shown in Figure 4.24. Kapton is a polyimide film composed of repeating units of pyromellitic dianhydride and 4,4'-oxydiphenylamine, with aromatic rings connected by imide linkages. Ethylcellulose is a carbohydrate polymer consisting of glucose units functionalized with ethyl groups. Terpineol is an alcohol-based solvent containing a hydroxyl group, while Cyclohexanol is a solvent with a hydroxyl group attached to a cyclohexane ring.

The peak at 1711 cm⁻¹ is consistent with the C=O (carbonyl) stretch of amide groups, falling within the typical range of 1700-1750 cm⁻¹. Kapton, being a polyimide, contains aromatic imide rings with carbonyl groups in its chemical structure. The peak at 1498 cm^-1 aligns closely with the 1480-1440 cm⁻¹ range associated with C=C vibrations. The aromatic C-C stretching vibrations can also occur in this range due to the presence of aromatic rings in Kapton. The peaks at 1377 cm⁻¹ and 1244 cm⁻¹ are less definitive in pinpointing specific functional groups and may be attributed to aromatic C-C stretching, C-N stretching (around 1375 cm⁻¹), or C-O-C stretching (around 1250-1050 cm⁻¹). The 1114 cm⁻¹ peak falls within the range (1124-1087 cm⁻¹) associated with C-O-C stretching vibrations.

The small peaks observed at 3096 cm⁻¹, 3660 cm⁻¹, and 2775 cm⁻¹ align with the typical ranges associated with O-H stretching vibrations. These findings suggest the possible presence of hydroxyl (OH) groups, likely attributed to either moisture adsorbed on the Kapton surface or trace impurities containing OH groups.

In Figure 4.23, similar peaks were observed in both the Kapton and AG samples, as expected due to the likely presence of similar chemical bonds and functional groups in both materials. The reduced intensity of the peaks in the AG samples, especially in the unannealed ones, suggests that the AG film is partly obscuring the Kapton signals, indicating a lower concentration of AG on the Kapton substrate compared to the Kapton itself.

It is probable that the concentration of C-O functionalities in the oxygenated 3D graphene is lower than the functionalities in Kapton. Therefore, no additional peaks due to functional groups in graphene are seen. The decrease in peak intensity in annealed AG samples may indicate gasification, i.e. species lost from the sample as CO, CO₂, H₂O, etc. Thermogravimetric analysis (TGA) was not performed to confirm this further.

It can be concluded that the distinct infrared (IR) signatures of the oxygen functionalities potentially present in the AG samples are challenging to distinguish. These signals are often masked by the more intense signals arising from the abundant functional groups within the Kapton substrate. This difficulty in differentiation underscores the need for alternative techniques with higher sensitivity towards these groups to gain a clearer picture of the oxygen functionalities in AG.

In an attempt to isolate the AG samples, flakes of the sample were extracted from the surface of the Kapton tape. Attenuated Total Reflectance (ATR) spectroscopy was then performed on the isolated materials. The resulting spectra are depicted in Figure 4.25.

The absence of Kapton film facilitates more explicit observation of the functional groups present in the AG flakes. The AG flakes were carefully removed from the surface by gently scraping the tape with a plastic spatula. It is important to consider that this method has the potential to introduce contaminants.

The spectra depicted in Figure 4.25 indicate the presence of oxygen functionalities, likely hydroxyl groups in graphene, hydroxyl groups of ethyl cellulose, or co-adsorbed water groups, as evidenced by a broad peak around ~3400 cm⁻¹. Additionally, a prominent peak at 1704 cm⁻¹ suggests the presence of carbonyl groups, which is worth highlighting. Moreover, the signals in the 2862-2933 cm⁻¹ range are sharp, indicating they are more likely associated with C-H stretching vibrations rather than O-H.

The spectra also confirm the presence of aromatic C-C stretching at 1448 cm⁻¹, confirming the existence of a graphene structure within the AG flakes. A peak at 1219 cm⁻¹ may suggest C-O stretching, although isolating specific oxygen-containing functional groups in the AG can be challenging due to the presence of multiple peaks and potential overlap with C-C stretching.

Similar observations have been made in recent studies. For example, graphene oxide (GO) and reduced graphene oxide (rGO) are reported to exhibit a broad O-H stretching vibration band, a carboxyl C=O stretching band, O-H deformation vibration, and C-O stretching vibrations.³⁴



Figure 4.25. The FTIR Spectrum of AG 0.5 and AG 0.75 Flakes Were Removed from Kapton and Analysed Using ATR.

XPS of AG samples on Kapton

XPS analysis was conducted on AG films with different levels of oxygen content (AG 0.3 - AG 0.75) that were printed on Kapton substrates. The purpose of the analysis was to characterise the elemental composition, with a specific focus on fitting the carbon (1s C), oxygen (1s O), and nitrogen (1s N) signals. It was determined that the nitrogen signal, originating from the nitrogen atoms in the Kapton substrate, comprised approximately 0.04 to 0.16% of the total chemical composition in each sample. Figure 4.27 shows the results for the annealed samples while Figure 4.28 displays the data for the unannealed samples.







Figure 4.27. XPS Analysis of Bonding C 1s Peaks in AG Films With Varying Oxygen Content of All the Annealed Samples

The XPS analysis of the Kapton substrate in Figure 4.26 shows the material's characteristic bonding environment. The presence of peaks at approximately 284.6 to 284.8 eV (C-C/C=C) and 286 to 286.6 eV (C=O) confirms the existence of aromatic and carbonyl groups in the Kapton structure, which aligns with its chemical composition, including pyromellitic dianhydride (PMDA), biphenyl tetracarboxylic dianhydride (BPDA), oxydianiline (ODA), and p-phenylenediamine (PPD), as illustrated in Figure 4.24.



Figure 4.28. XPS Analysis of Bonding 1s Peaks in AG Films with Varying Oxygen Content (Unannealed)

% Carbon								
		C type						
Condition		C-C C=C	С-ОН, С- О-С	C=0	0-С-ОН	π-π*		
	Sample		Bindin	g Energies (eV)			
		~284.6 to 284.8	~284.9 to285.9	~286 to 286.6	~286.4 to 288.9	~290		
Annealed	AG 0.3	49.65	27.87	11.97	_	10.50		
Unannealed	AG 0.3	40.24	24.86	24.87	6.84	3.19		
Annealed	AG 0.4	34.99	30.93	19.91	_	14.17		
Unannealed	AG 0.4	39.02	24.27	17.70	15.72	3.39		
Annealed	AG 0.5	50.27	23.91	17.39	_	8.43		
Unannealed	AG 0.5	19.55	24.58	47.01	8.87	_		
Annealed	AG 0.75	31.45	38.23	21.11	_	9.21		
Unannealed	AG 0.75	30.59	45.89	23.52				
n/a	Kapton Substrate	48.25	40.37	_	11.37	_		

Table 4.18 XPS fitting of the % Carbon according to C 1s binding energies (eV) of all AG samples and Kapton.

Based on the XPS analysis of all AG samples that were annealed and unannealed, as well as the clean substrate Kapton, as shown in Table 4.18, some noticeable trends can be observed with increasing oxygen content. Specifically, there is a decrease in the percentage of C-C and C=C bonds (284.6 to 284.8 eV and 284.9 to 285.9 eV, respectively) with increasing oxygen content. Conversely, an increase in the percentage of C-OH and C-O-C bonds (284.9 to 285.9 eV) is observed. Additionally, there is a decrease in the percentage of C=O bonds (286 to 286.6 eV) with increasing oxygen content, while an increase in the percentage of O-C-OH bonds (290 eV) is also observed.

Unannealed samples exhibit a wider range of bonding configurations, as shown in Figure 4.28, with broader or more complex C 1s peaks compared to the annealed samples. This can be attributed to the presence of the surfactant. The unannealed samples contain surfactants, which were not removed prior to the printing of the films. The presence of these surfactants suggests that there are likely to be more oxygen species present. In this case, ethylcellulose served as the surfactant, and the solvents used were cyclohexanol and terpineol. The chemical structures of ethylcellulose, cyclohexanol, and terpineol are shown in Figure 4.24. Ethylcellulose surfactant is a carbohydrate consisting of polymeric chains of glucose units functionalized with ethyl groups. Therefore, it contains sp³ carbons and C-O bonds, which may contribute to the intense peaks in the XPS spectra corresponding to C(sp³), C-O, and C-OH.

The XPS measurements were performed twice for a few samples, but not all samples, to ensure reproducibility, and the results showed consistent trends with some variation in the unannealed samples. The increased variation in unannealed samples may be attributed to the presence of co-adsorbed ethylcellulose, which is removed upon annealing. This could explain the prominent C-O peak in AG 0.5 and the broad C-C peak in AG 0.75. Since AG 0.5 and AG 0.75 are more highly oxygenated than AG 0.3 and AG 0.4, they are expected to bind ethylcellulose more strongly, which may indicate that these spectra contain signals of ethylcellulose.

Oxygen can bond to the edges or basal plane of the graphene sheet, introducing functional groups like C-OH, C-O-C, and O-C-OH. These groups significantly impact the electronic properties of graphene by introducing new electronic states and potentially introducing band gaps and shifting the Fermi level. The presence of oxygen functional groups can break the symmetry of the graphene lattice and introduce energy levels within the conduction and valence bands. This would disrupt the free movement of electrons.

As the concentration of oxygen rises, there is an increased ability for oxygen to form bonds with the carbon atoms in the graphene lattice, leading to the formation of defects. These defects have the effect of disrupting the carbon network, thereby modifying the overall quality of the film. In Raman spectra, the presence of defects is often associated with the intensity of the D peak, where a higher D/G peak ratio is indicative of greater defect densities in graphene.³⁵

The observed changes in percentages of different carbon environments as a function of oxygen content indicate that all AG samples contain a relatively low proportion of sp²-bonded carbon atoms compared to the 100% expected in pure graphene. This suggests the presence of a significant amount of oxygen in the samples. Furthermore, the data confirm that the percentage of oxygen increases from AG 0.3 to AG 0.75, as expected. However, it is important to address the anomaly seen in AG 0.5, which does not follow the expected trend. In the literature, it is well-documented that XPS measurements of oxygen in carbon-rich materials can be challenging and often unreliable due to surface contamination and measurement sensitivities.³⁶ Additionally, we do not anticipate more than 1% oxygen content from doping alone. In short, while XPS data broadly suggest a trend (with AG 0.5 being an outlier), the absolute oxygen proportions are likely exaggerated.

4.2.3.4. AFM

The utilisation of AFM allowed for the measurement of sample thickness, facilitating an examination of the correlation between film thickness and its absorption spectrum. By precisely quantifying thickness, we can gain insights into how the number of printed passes impacts the final film thickness as well as its optical and electronic properties. This comprehension is vital for optimising the efficiency and performance of these films in various applications.

For sample 0.7 (3 printed passes), the average thickness was determined to be 1.65 μ m (σ = 0.07 μ m), whereas sample 0.5 (3 printed passes) exhibited an average thickness of 0.9 μ m (σ = 0.08 μ m). Despite the same number of printing passes, the variance in thickness implies that factors beyond the number of layers, such as material concentration, deposition technique, or the presence of surfactants, significantly influence the final film morphology. The unexpectedly large thickness, far exceeding the anticipated range of 3-6 nm for an estimated ~20-layer graphene film, suggests the presence of a substantial surfactant layer within the samples or possible presence of contaminants.

4.2.4. Discussion

XPS and FTIR analysis provided evidence for the incorporation of oxygen into the AG films. Furthermore, a direct correlation was established between increasing oxygen content and a decrease in C-C bonds. Conversely, the presence of oxygen-containing functional groups (C-OH, C-O-C, O-C-OH) increased with higher oxygen content. These functional groups are known to introduce defects and significantly impact the electronic properties of the AG films.³⁷

A clear correlation emerged between oxygen content and relaxation timescales. Films with lower oxygen content (AG 0.3) exhibited longer decay times compared to their higher oxygen content counterparts (AG 0.75). This suggests a process of slower carrier cooling within the films containing less oxygen. The presence of multiple decay components in the relaxation profiles indicated the existence of complex relaxation processes occurring within the AG films. Notably, the number of these components varied depending on the oxygen content and the experimental time window. Reflectance measurements provided information about the surface region of the films, while transmittance probed the entire film volume.

While both techniques revealed similar trends in relaxation behaviour at early times, some differences were observed in the later stages. For example, AG 0.3 exhibited a longer τ 3 in reflectance compared to transmittance, highlighting variations between surface and bulk relaxation processes. AG 0.5 also showed a notable difference with a longer τ 3 in transmittance versus reflectance. These differences suggest distinct dynamics at the surface and within the bulk of the films.

This study effectively demonstrates the influence of oxygen content on the electronic properties of AG films deposited on Kapton substrates. By carefully controlling the oxygen content during the fabrication process, it becomes possible to tune the relaxation behaviour and electronic characteristics of these graphene films, that could possibly be used for sensing devices.

The most optimal samples for analysis were the annealed and diluted ones, which had fewer printed layers. These samples exhibited greater transparency and uniformity. Despite the numerous variations in this batch, the Kapton tape substrate proved to be highly flexible and potentially valuable for device applications. However, the printed G and AG films showed poor adhesion to the tape, with some flaking or rubbing off in certain cases. This presented challenges for longer experiments such as TA, but was useful for performing FTIR analysis as the AG flakes could be extracted. Furthermore, the weak adhesive property of the substrate tape made it challenging to place it on sample holders. The films also appeared excessively dark on the Kapton surface due to its dark yellowish colour, complicating most measurements. In light of the observed challenges, the research team opted to revert to utilising quartz substrates for sample printing throughout the remaining duration of the project. Although Kapton was initially considered a suitable substrate due to its flexibility and ultra-thin nature, its yellow colour could have interfered with spectroscopic investigations.

4.3. SAMPLE SET 3: DILUTED GRAPHENE AND AEROGEL GRAPHENE WITH VARYING OXYGEN CONTENT PRINTED ON QUARTZ

4.3.1 Sample Description

The third set of samples comprised four diluted aerosol gels and one graphene film, represented as AG and G, respectively, printed on quartz substrates. These films contained varying oxygen-to-carbon ratios (O/C). The samples were prepared using the same technique as batch 1.

4.3.2 Characterisation Methods

A wide range of characterisation methods were utilised to examine the properties of the printed films comprehensively.

4.3.2.1. Scanning Electron Microscopy (SEM)

SEM imaging was conducted at Kansas State University to analyse printed graphene and graphene aerosol gel films. The SEM imaging parameters used were a 5.0kV accelerating voltage and a 4.9mm x 50.0k magnification.⁶

4.3.2.2. Transmission Electron Microscopy (TEM)

Five samples, one pristine graphene and four AG containing varying oxygen levels (0.3, 0.4, 0.5, and 0.75), were analysed using TEM at the Henry Royce Institute. The analysis employed a JEOL JEM-2100 microscope equipped with a LaB6 filament source, an Oxford Instruments EDS detector for elemental analysis, and a Gatan Orius CCD camera for image capture. The imaging was performed with an accelerating voltage of 80 kV.³⁸

4.3.2.3. UV-Vis Spectroscopy

Measurements were taken using an Agilent Cary 60 UV–vis spectrometer using the same method and apparatus as other batches.⁷

4.3.2.4. Pump-Probe Spectroscopy (UV and NIR)

The pump-probe spectroscopy experiments were conducted at the Lord Porter Ultrafast Laser Laboratory, employing the Helios system, similar to the experiments for batch 1 samples. The laser source and initial pulse generation were consistent. Frequency doubling resulted in 400 nm pump pulses (2.5 kHz, 0.2 μ J) focused onto the sample with a smaller diameter of approximately 150 μ m.

A notable difference in this experiment was the probe; in addition to the UV-Vis white light continuum, a sapphire crystal generated an NIR probe continuum of 850-1600 nm. A CMOS camera with a 1.5 nm resolution measured the intensity of both transmitted probe signals. The remaining setup mirrored experiments for batch 1, and data were analysed using the same fitting procedure as previously stated.

4.3.2.5. Surface and Depth Analysis: X-ray Photoelectron Spectroscopy (XPS)

The methodology employed for the analysis of batch 3 samples closely followed the procedure outlined in section 4.1.2.3. Notably, this batch underwent a high-resolution scan for the carbon (1s) peak, which facilitated comprehensive surface and depth analysis, yielding a more detailed insight compared to previous analyses.

4.3.2.6. Surface Analysis: Profilometry

Surface profiles of the samples were measured at the Henry Royce Institute at the University of Sheffield, Department of Materials, using a Bruker Contour GT-I Optical Microscope (Model 831-775) equipped with an OpticalProfiler.³⁹

4.3.2.7. Material Characterisation: Scanning Near-Field Infrared Microscopy (SNOM) with Atomic Force Microscopy (AFM)

The samples labelled AG and G underwent high-resolution imaging and scanning using both Scanning Near-field Optical Microscopy (SNOM) and Atomic Force Microscopy (AFM). AFM accurately mapped surface features and provided detailed profiles of the thickness of the samples. SNOM, which utilised infrared light, probed the samples and identified unique vibrational signatures. This experiment was carried out at the specialised facility of the University of Sheffield under the guidance of Dr. Alex Knight. The study leveraged Fourier Scan mode, a mid-infrared laser source, and high-resolution scanning capabilities.⁴⁰

4.3.2.8. Raman Spectroscopy

Raman analysis was conducted after the fabrication of the printed samples at Kansas State University. $^{\rm 41}$

4.3.3. Results

4.3.3.1. SEM

The surface morphology of the G and AG films was examined through scanning electron microscopy (SEM), a high-resolution imaging technique providing an in-depth understanding of surface texture, features, and potential compositional or structural variations. The analysis demonstrates a clear relationship between oxygen content and particle size. Compared to pure graphene, the AG samples exhibited noticeable changes in particle size. Pure graphene displayed a flatter appearance, suggesting a more uniform and well-defined structure, while the AG samples showcased smaller and more diverse particle sizes. The particle size range for the AG samples shown in Figure 4.29 ranges from 0.1 μ m for AG 0.3 to 0.4 μ m for AG 0.75.



Figure 4.29. SEM Images of G and AG Samples. All Images have the same magnification and resolution for clear comparison.

The observations provided in Figure 4.29 offer compelling experimental evidence regarding the influence of oxygen on the morphology of graphene. The introduction of oxygen is likely to disrupt the ordered structure of pure graphene, thereby resulting in the formation of more irregular particles and flakes within the AG films. This analysis aligns with concepts discussed in past research papers. A study by Hummer in 1958 describes the exfoliation process caused by oxygen functional groups. This separation created individual sheets or flakes of graphene oxide.⁴² A more recent study from 2021 highlights how oxygen disrupts the strong sp² bonds within pristine graphene. This disruption weakens the forces holding the graphene layers together, ultimately leading to the formation of individual flakes.⁴³ Further investigation, explicitly focusing on detailed height measurements, could yield a more comprehensive understanding of the AG films' surface topography and three-dimensional structure.

4.3.3.2. TEM

TEM analysis obtained high-resolution microstructural information about the films at the atomic scale. In addition, Electron Energy-Loss Spectroscopy (EELS) was also attempted. However, the experiment did not produce the desired results due to a malfunction in the EELS equipment.

EELS is a highly effective technique for obtaining detailed information about the chemical composition, electronic structure, and bonding environment of materials at the nanoscale. By examining the energy lost by electrons as they traverse a sample, EELS can provide valuable insights into the elemental composition, chemical bonding, electronic structure, and thickness of graphene derivative samples.⁴⁴

TEM image of the pure graphene film in Figure 4.30 revealed its characteristic honeycomb structure, allowing for a direct view of the arrangement of carbon atoms at the atomic scale. The examination of the printed AG films using TEM revealed a structurally complex and three-dimensional arrangement distinct from the flat graphene film. The images illustrate crumpled nanosheets resembling graphene for low O/C, while higher O/C exhibits nano-shells and curved graphene. Additionally, it could be argued that evidence of a turbostratic structure was observed in the AG samples. This indicates that the AG film comprises multiple graphene layers stacked with some rotation between them. This rotational disorder does not significantly reduce carrier mobility because it minimises interlayer coupling, allowing each graphene layer to conduct electricity similarly to single-layer graphene.⁴⁵ The TEM images were taken from both side and top views. The side views reveal that the graphene is curved but do not explicitly show whether the layers are rotated relative to each other. The top views provide insights into the in-plane arrangement of the layers, offering a more comprehensive understanding of the material's structure.

In contrast to regular multilayer graphene with a perfect stacking pattern, known as Bernal stacking, turbostratic graphene displays rotational disorder, with each layer slightly rotated relative to its neighbouring layers. The TEM images revealed a range of layer numbers within the AG samples, with most stacks comprising approximately 10 to 30 graphene layers. However, some rare cases showed around 6 to 8 layers, and in certain instances, stacks with more than 30 layers were observed. The average interlayer spacing was measured to be approximately 0.333 nm, which is typical for graphene and aligns with values reported for turbostratic and multilayer graphene. This disruption of orbital hybridisation results in electronic properties similar to single-layer graphene, including potentially high electrical conductivity.⁴⁶ Larger TEM image scans of select fee samples can be found in the appendix.

The potential to achieve good electrical conductivity with multiple layers presents advantages in material production and device design. When the rotation angles between layers fall within a specific range, the material can exhibit metallic behaviour, meaning it readily conducts electricity. Unlike single-layer graphene, which can be challenging to produce in large quantities, turbostratic graphene offers a more practical option while still delivering comparable electrical performance.⁴⁷

According to the recent literature, the stacking arrangement of atoms in a graphene and graphene van der Waals heterostructure, also known as double-layer graphene, significantly impacts its electrical properties.⁴⁸ In regular graphene, electrons move within a single layer with energies in the range of electron volts (eV). When stacked as a double layer, the movement of electrons between the layers involves much lower energies, in the range of hundreds of millielectronvolts (meV). Unique bilayer graphene structures were created by rotating one layer of graphene relative to the other.⁴⁹ This twist disrupts the perfect alignment of atoms in the layers, leading to important effects. The rotation creates a prominent, repeating pattern of overlapping atoms called a Moiré superlattice. The twist misaligns the energy levels (bands) where electrons reside in each graphene layer. This increases the size of the unit cell representing the structure.⁴⁹ The combined effects of the Moiré superlattice and modified band structure have a dramatic impact on the electrical behaviour of Twisted Bilayer Graphene (TwBLG). The twist enhances the interaction between electrons in the double layer, creating

two distinct electron states. Under specific circumstances, this strong interaction can also induce a superconducting state, where electrons exhibit zero resistance while flowing.⁵⁰ The irregular stacking observed in the AG samples could resemble the TwBLG structure, suggesting that similar electronic phenomena might occur.



Figure 4.30. TEM Images of all AG Samples and 1 G Sample All Images Have the Same Resolution.

4.3.3.3. UV-VIS

Figure 4.31 presents the UV-visible transmission spectra of the inkjet-printed graphene films (G and AG 0.3–0.75). Similar to the results in sections 4.1 and 4.1, graphene (G) demonstrates a wide absorption range between 200-800 nm, with the lowest transmission occurring at 267 nm. All AG films exhibit a broader transmission spectrum than G, with AG 0.75 showing the most significant broadening. AG 0.3-0.5 films have transmission minima at 253 nm, slightly shifted towards the blue compared to G, and consistent with previous batch one AG films. On the other hand, AG 0.75 has a notably broader spectrum with a less prominent minimum at 272 nm.



Figure 4.31. UV-vis Transmission Spectra of Ink-Jet Print Aerosol Gel Graphene Films, with Varying O/C Ratio, and a Pristine Graphene Film (left). Normalised Graph of the UV-Vis Absorption Spectra (right)

Table 4.19 Optical Properties of Batch 3 Samples

Sample	%T (800 nm)	number of estimated layers
G	67.14	17
0.3	54.07	26
0.4	69.54	16
0.5	66.26	18
0.75	61.60	21

The increase in spectral broadening observed in AG films may be linked to variations in the particle size of graphene oxide (GO) flakes present in the inks. As the oxygen-to-carbon ratio (O/C) rises, the size of suspended GO flakes also increases, potentially resulting in a larger scattering cross-section in the printed films and impacting their overall transmission properties. Similar to batch 1 samples, the number of estimated layers of each sample has been calculated in Table 4.19, suggesting an average of ~20 layers for each sample.

The observed absorption peak around 270 nm can be ascribed to the π - π^* transition in aromatic systems, prevalent in graphene and its derivatives like GO and reduced GO. This transition involves the excitation of an electron from a bonding π orbital to an antibonding π^* orbital, essentially promoting an electron from the valence band to the conduction band. This electronic transition is associated with ultraviolet light absorption, typically around 260-270 nm, and contributes to the characteristic color of graphene-based materials.



Figure 4.32. (a) UV-Vis Absorbance Comparison of Samples from Batch 1 and Batch 3, (b) Comparison of Absorbance on Sample AG 0.75 at Different Positions of the Film

The UV-Vis absorbance spectra of samples from two distinct batches, batch 1 and batch 3, were analysed for comparative purposes to assess the similarity between the batches. Figure 4.32 (a) illustrates that the AG 0.5 sample from batch 3 and the AG sample from batch 1, which were confirmed by collaborators to have identical oxygen content, displayed remarkably similar UV-Vis absorbance spectra. This similarity indicates a close resemblance in their overall chemical composition. Furthermore, the G samples from both batches exhibited analogous absorbance peaks, suggesting a high degree of consistency in their sp² carbon network structure. These findings imply a high level of control and reproducibility in the production process for both AG and G samples across the two batches.

The comparison of absorbance at various positions of the AG 0.75 film, as illustrated in Figure 4.32 (b), is essential for evaluating the film's uniformity. This analysis aids in establishing whether the film exhibits consistent properties across its surface. The absorbance spectra reveal minimal deviations among different positions, suggesting a uniform film characterised by homogeneous chemical composition and consistent properties.

Estimated Band Gaps via Tauc Plots

Using a method described in a research paper in 2018,⁵¹ the Tauc plots for the AG samples were generated. The data was collected as percentage reflectance (%R vs nm) on quartz substrates, and the Tauc method was employed to estimate the optical bandgap of the samples. For a detailed explanation of the Tauc plot theory and the calculation method, please refer to Appendix Section 10.3.

Based on the analysis of these plots, the AG samples appear to exhibit an indirect bandgap transition, as shown in Figure 4.33, with bandgaps for the main transition of between 2.1-2.5 eV. This suggests that these materials' momentum requirements for the most intense electron excitation involve phonon interactions. The estimated bandgap energies are shown in Figure 4.33 indicate that an increase in oxygen content leads to a slight decrease in band gap energy.



Figure 4.33. Tauc Plots for Batch 3 AG Samples Printed on Quartz, Showing the Estimated Band Gaps Calculated Using the Indirect Bandgap Method.

4.3.3.4. Transient Absorption Spectroscopy Results

The changes in transmission ($\Delta T/T$) of all the samples after being excited with a 400 nm laser pulse are displayed in Figure 4.34 (right). The changes are shown in both the visible range from 420 nm to 690 nm and in the near-IR spectral regions from 850 nm to 1600 nm. Right after being excited, all the films show a positive $\Delta T/T$ signal across the entire spectral range of the transient experiments. This signal is attributed to photobleaching, which is the fading of the broad ground-state absorption band due to the depletion of the available valence to conduction band electronic transitions.



Figure 4.34. (left) Graphs Depict the Dependence of Carbon-Optical Phonon (C-OP) Scattering Rates on the Wavelength of the Incident Probe Light. (right) Transient Changes in Transmission (ΔT/T) of G and AG 0.3–0.75, Following Excitation at 400 nm, in the Spectral Regions 420–690 nm and 850–1600 nm. Pump-probe time delays span -100 to 1500 fs.

In all films, the highest positive signal in the visible region (500–650 nm) is achieved with a pumpprobe delay, or t_{max} , of 65 fs. However, t_{max} for probe wavelengths below 500 nm increases to approximately 80 fs. This variation is likely due to the contribution of the coherent artefact signal from the quartz substrate to the overall $\Delta T/T$ signal across the visible region. At shorter wavelengths (<500 nm), the magnitude of the coherent artefact signal and sample signal become comparable. On the other hand, in the near-IR region, t_{max} shows significant dependence on the probe wavelength in all samples, increasing as the probe wavelength increases, except for AG 0.75. The observed variation is as large as 180 fs for AG 0.5. The graphs of t_{max} against wavelength for these samples can be found in the appendix.

The delay in reaching the maximum $\Delta T/T$ signal for longer wavelengths may be partly attributed to the initial negative $\Delta T/T$ signal in the region >1400 nm for AG 0.3, 0.4, and 0.5, which overlaps with the increasing positive signal. The coherent artefact signal from quartz is initially negative at time zero, but its magnitude is not sufficient to account for the observed $\Delta T/T$ response, suggesting that the negative signal also originates from the sample. Furthermore, the delayed appearance of the signal in the near-IR region, relative to the visible region, could indicate the time required for carriers to equilibrate at energies significantly lower than those of the initially photo-injected carriers.

The initial positive signal decay is significantly influenced by the probe wavelength across all samples; the positive $\Delta T/T$ signal's decay time grows longer with increasing probe wavelength. Since the scattering rate is inversely proportional to the decay time (τ_{max}), this implies that the scattering rate decreases as the probe wavelength increases. The scattering rates of carrier optical phonons, which

reflect the energy dissipation due to carrier-phonon interactions, are depicted in Figure 4.34 (left) as a function of the probe wavelength. These scattering rates can be estimated using the relation scattering rate $=\frac{1}{\tau_{max}}$, where τ_{max} is the time for the maximum positive $\Delta T/T$ signal to decay.

Kinetic Traces, UV and NIR

Kinetic traces at 550 nm and 1550 nm for the AG films are depicted in Figure 4.35. In the time range of 50–1500 fs, the initial bleaching signal at 550 nm fully decays for all samples, with AG 0.75 showing a notably faster decay, reaching baseline within 90 fs. The extracted lifetimes are presented in Table 4.20 for 550 nm and Table 4.21 for 1550 nm. Exponential fittings at 550 nm indicate decay times of approximately 110-120 fs for G, AG 0.3, 0.4, 0.5, while AG 0.75 decays faster with a lifetime of less than 90 fs. As seen in Figure 4.35, at 1550 nm, the decay of the bleach signals occurs more gradually, with slower rates compared to λ =550 nm for all samples. This indicates slower carrier optical phonon scattering rates at lower carrier energies. Despite the slower visual decay at 1550 nm, the decay at this wavelength. A small negative signal is observed around time zero for AG 0.3–0.5, which shows ultrafast temporal dynamics.

To summarise quantitatively, at 1550 nm, G has a decay time (τ 1) of 58 fs, AG 0.3 shows 85 fs, AG 0.4 has 79 fs, AG 0.5 shows 121 fs, and AG 0.75 has a longer decay time of 339 fs (Table 4.21). These lifetimes are considerably shorter than those at 550 nm, which could correspond to the fact that even though the decay visually appears slower, the lifetimes represent early, rapid decay components in multi-exponential fits.



Figure 4.35. Normalised Single Point Kinetic Traces at 550 nm (left) and 1550 nm (right), for All Samples, Overlaid with their Exponential Fits.

Kinetic lifetimes at 550 nm								
	sub-p	sub-ps (ps) growth neg. signal (ps)		recovery (ps)		recovery		
sample	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3 (ps)	τ3 error	τ4 (ps)	τ4 error
G	0.114	0.003	0.643	0.092	13.530	3.509	8	0
0.3	0.115	0.002	1.643	0.755	6.651	7.579	∞	0
0.4	0.114	0.002	1.421	0.381	10.104	8.671	∞	0
0.5	0.120	0.002	0.690	0.258	54.206	26.386	8	0
0.75	0.086	0.008	0.699	n/a	1.006	n/a	8	0

Table 4.20 Lifetimes of all samples at 550 nm (UV-Vis)

Table 4.21 Lifetimes of all samples at 1550 nm (NIR)

Kinetic lifetimes at 1550 nm								
	sub-ps (ps) growth neg. signal (ps) recovery (ps) recovery							
sample	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3 (ps)	τ3 error		
G	0.058	0.007	0.436	0.013	∞	0		
0.3	0.085	0.009	0.255	0.022	1.597	0.192		
0.4	0.079	0.005	0.290	0.017	1.805	0.298		
0.5	0.121	0.010	0.290	0.047	1.085	0.128		
0.75	0.339	0.015	2.138	0.262	n/a			

Magnitude of the Long-Lived Signal

A long-lived transient signal is linked to absorption caused by the existence of trapped electronic states. Previous research in section 4.1 emphasised the presence of trapped states in the aerosol gel graphene films, but absence of such states in pure graphene films.¹ Figure 4.36 illustrates the dynamic behaviour of the photoinduced absorption (negative $\Delta T/T$) up to pump-probe delays of 80 ps for all the samples.



Figure 4.36. Kinetics Traces at 550 nm, Both Normalised (right) and Unnormalised (left), Highlighting the Recovery Dynamics of the Negative ΔT/T Signal.

The kinetic traces depicted on the left side of the figure represent the unnormalised data, whereas the graph on the right showcases the traces normalised to the initial maximum positive signal. Normalised to the max positive signal, representative of the number of initial charge carriers generated, and hence, representative of the energy deposited. This normalisation enables a direct comparison of the magnitude of the negative signal across different samples, accounting for variations in optical densities at the excitation wavelength. The normalised data reveals a discernible trend in the magnitude of the negative signal: notably, the signal of G exhibits a negligible value at 80 ps, while the quasi-stationary signal for the aerogel films increases as the oxygen-to-carbon ratio rises from 0.3 to 0.75. Consequently, the present data reinforces the idea that the concentration of trapped carriers grows in tandem with the increasing oxygen-to-carbon content.

Lifetimes and Recovery at Different Wavelengths

Lifetimes presented in Table 4.22 show that there is a noticeable correlation between increasing wavelength and extended lifetime across the tested materials. This pattern holds true for both graphene and all AG samples. As the incident light's wavelength changes from 450 nm to 1500 nm, the associated recovery lifetime also increases for all systems. This phenomenon can be linked to the energy-dependent nature of carrier recombination processes in semiconductors. Signals at shorter wavelengths, within the UV region, correspond to higher energy transitions. The population of these higher energy states has a broader range of lower energy states available to transition to, thus expediting recombination processes. As a result, shorter lifetimes are observed at shorter wavelengths. Conversely, longer wavelengths within the NIR region correspond to lower energy photons. The population of these lower energy states possess fewer accessible low-energy states leading to recombination. Consequently, the excited electrons must await suitable holes for a longer duration, leading to slower recombination processes and, consequently, longer lifetimes at longer wavelengths.

The data indicate that the overall recovery times for all AG variations exceed that of pristine graphene. Pristine graphene, known for its outstanding conductivity and low defect density, demonstrates shorter lifetimes owing to efficient carrier transport and recombination. However, in AG the pristine structure is disrupted by oxidation, which introduces additional energy states within the bandgap of graphene. This phenomenon creates new pathways for non-radiative recombination, leading to a longer recombination time for electrons and resulting in increased lifetime for AG compared to G. The impact of oxidation on the band gap of graphene is further examined computationally in Chapter 5. Moreover, the defects caused by oxidation can serve as traps for excited carriers, temporarily delaying their recombination with holes (vacant electron states). Subsequently, the trapped carriers may either recombination process and extending the lifetimes, consistent with previous observations in this chapter.

Wavelength				G	ì				
(nm)	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3	τ3 error	τ4 (ps)	τ4 error	
500	0.087	0.004	0.438	0.110	14.099	2.921	∞	0	
550	0.114	0.003	0.642	0.099	15.235	4.978	∞	0	
600	0.129	0.004	0.736	0.162	12.172	6.134	~	0	
1105	0.280	0.009	1.674	0.133	n/a		n/a		
1300	0.350	0.016	3.609	3.335	~	0	n/a		
1500	0.389	0.016	3.060	1.247	∞	0	n/a		
Wavelength		AG 0.3							
(nm)	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3	τ3 error	τ4 (ps)	τ4 error	
450	0.075	0.001	5.483	4.830	11.941	9.117	∞	0	
500	0.097	0.001	2.197	0.572	10.360	4.372	∞	0	
550	0.115	0.002	1.643	0.754	6.655	7.582	~	0	
600	0.130	0.003	2.694	19.279	3.240	28.289	~	0	
1105	0.254	0.016	1.263	0.578	~	0	n/a		
1300	0.340	0.014	3.410	1.895	~	0	n/a		
1500	0.372	0.020	3.020	1.306	∞	0	n/a		
Wavelength		<u>.</u>		AG	0.4				
(nm)	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3	τ3 error	τ4 (ps)	τ4 error	
450	0.082	0.001	3.805	1.758	13.086	6.429	∞	0	
500	0.099	0.001	1.935	0.561	12.082	6.803	×	0	
550	0.114	0.002	1.421	0.381	10.105	8.671	∞	0	
600	0.130	0.003	3.033	32.844	3.438	43.926	~~	0	
1105	0.308	0.007	3.164	1.523	~	0	n/a		
1300	0.350	0.016	3.609	3.335	~	0	n/a		
1500	0.389	0.016	3.060	1.247	∞	0	n/a		
Wavelength				AG	0.5				
(nm)	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3	τ3 error	τ4 (ps)	τ4 error	
550	0.120	0.002	0.731	0.274	51./61	24.652	~	0	
600 1105	0.122	0.002	0.508	0.145	/6.282	47.583	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	U	
1200	0.208	0.010	1.014	0.042	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0	n/a		
1500	0.349	0.011	3.103	2.009	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0	n/a		
1500	0.396	0.017	2.344	0.914	~	0	n/ a		
wavelength	-1 (_1	-2 (AG (-2		-4 (
(nm)	τι (ps)	ti error	τ2 (ps)	t2 error	τ3	τ3 error	τ4 (ps)	τ4 error	
450	0.054	0.002	1.748	0.246	~	0	n/a		
500	0.077	0.001	2.093	0.201	~	0	n/a		
550	0.098	0.001	1.853	0.179	~	0	n/a		
600	0.100	0.002	1.819	0.327	∞	0	n/a		
1105	0.224	0.008	1.652	0.352	∞	0	n/a		
1300	0.363	0.014	0.001	4.03E+08	∞	0	n/a		
1500	0.369	0.022	3.523	2.340	∞	0	n/a		

Table 4.22 Wavelength-Dependent Recovery Lifetime in Graphene and AG 0.3-0.75

Power Dependence Study for Sample AG 0.75 at 525nm (UV)

The following section illustrates the power dependence of the transient signal of sample AG 0.75, which possesses the highest oxygen content. Figure 4.37 illustrates a negative peak in the signal, which occurs at progressively later times with increasing fluence. This peak represents the maximum change (Δ T) associated with the excited state population in the film. The decay curve for the highest fluence at 1600 mJ cm⁻² appears to deviate from a simple monoexponential decay, indicating the presence of multiple decay processes with different timescales contributing to the overall signal recovery.

The observed shift in the peak position towards later times with increasing fluence indicates a longer lifetime for the excited states in the graphene film, leading to a slower decay of the ΔT signal. The data suggests that the excited state lifetime in the film increases in the sub-picosecond range as the intensity of the excitation pulse (higher fluence) increases.



Figure 4.37. Fluence Dependence of Excited State Lifetime in Aerosol Gel Graphene 0.75 Film (right) Zoomed in to 0 - 4 ps.

The instrument response function (IRF) can have a significant impact on the measured signal at lower fluences, particularly around time zero. The IRF, characterised by its Full Width at Half Maximum (FWHM), defines the system's temporal resolution. Under these circumstances, the IRF can distort the true signal and complicate the accurate extraction of fast decay components. The FWHM is a widely used parameter for accounting for the system's response time in ultrafast spectroscopy setups. Therefore, it is essential to consider this factor when interpreting early-time dynamics to prevent misinterpretation of rapid features in the transient signal.

4.3.3.5. XPS Results

The detailed XPS analysis of all AG samples, depicted in Figure 4.38, demonstrates a consistent trend across the samples. It indicates that the relative concentration of carbon-oxygen functional groups (C-OH, C=O) rises in relation to C-C bonds as the overall oxygen content in the films increases. This observation aligns with the anticipated incorporation of oxygen during film processing. However, the observed increase in silicon content based on XPS data necessitates further investigation. As the films are deposited on a quartz crystal substrate (SiO₂), it is likely that the silicon peak originates from the underlying substrate rather than the film itself. This suggests that the increasing silicon signal may not reflect a change in the film's composition.

Additionally, a portion of the oxygen signal could be attributed to the quartz substrate or surface contamination. XPS probes samples to a depth of several nanometres, focusing primarily on analysing the surface region. Hence, oxygen contamination on the film's surface or inherent oxygen within the quartz substrate could contribute to the overall observed oxygen signal.



Figure 4.38. XPS of all AG Samples with Varying Oxygen Content. Orange Graphs Depict the Carbon Fitting, and the Blue and Green Graphs Show the Fitting of Oxygen and Silicon, Respectively. (a) AG 0.3, (b) AG 0.4, (c) AG 0.5 and (d) AG 0.75.

Table 4.23 provides an overview of the binding energies observed for various elements and their corresponding bonds in all samples, as illustrated in Figure 4.38. A key observation is the presence of two distinct O 1s peaks in the AG 0.3, AG 0.4, and AG 0.5 samples. These two peaks correspond to different oxygen environments, likely related to O-C and possibly either O-Si or C=O bonds. This is consistent with the C 1s data, which suggests the presence of two C-O environments in these samples. In contrast, the AG 0.75 sample exhibits a single O 1s peak at an intermediate binding energy. While this peak could be a combined signal from oxygen within the film and oxygen from the underlying quartz (SiO_2) substrate, it is more challenging to assign specific oxygen environments based on this data. The larger particle size and higher oxygen content inferred from the C 1s analysis in AG 0.75 may further complicate the interpretation of the O 1s peak. Therefore, focusing on the more apparent distinction of the two O 1s peaks in AG 0.3, AG 0.4, and AG 0.5 allows for a better understanding of the chemical bonding environments in these samples.

Elements/Bonds	Binding Energies (eV)
Carbon	
C-C	~284.4 to 284.8
С-ОН, С-О-С	~284.9 to 285.9
C=0	~286.0 to 286.6
C=C	~284.6 to 285.0
π-π*	290.0
Oxygen	
C=0	~531.5 to 532.0
O-C-OH	~~533.0
Silicon	
SiO2	103.5
Organic Si	102.0

Table 4.23 XPS Binding Energies (eV) for Carbon, Oxygen, and Silicon for AG samples ⁵²

4.3.3.6. Profilometer

The thickness of the AG samples were analysed using a profilometer, and the details are recorded in Table 4.24. The thickness of the samples, as measured by a profilometer, is important for specific applications and desired properties of the films. The electronic, optical, and mechanical properties of graphene films are strongly influenced by the number of layers present in a sample. As a result, the dimensional characterisation of graphene films is crucial, especially with the continued development of new synthesis methods and applications.⁵³ In particular, graphene films show distinct electrical properties based on their thickness. Monolayer graphene has the highest electrical conductivity, while bilayer and few-layer graphene exhibit different band structures and electrical behaviour compared to monolayer.⁵⁴

Studies have consistently established a direct relationship between the oxygen content in GO and rGO and their structural characteristics. In oxygen-functionalized graphene, a correlation has been observed between the oxygen-to-carbon ratio (O/C ratio) and the thickness of GO. The O/C ratio serves as an indicator of the degree of oxidation within the GO lattice. Increased oxidation results in a higher O/C ratio, which signifies more oxygen atoms incorporated into the graphene structure and influences the d-spacing of GO. D-spacing refers to the separation distance between adjacent atomic layers within a material. In GO, introducing oxygen-containing functional groups, such as hydroxyl and epoxides, disrupts the pristine graphene structure and acts as spacers that separate individual graphene sheets. Consequently, a higher O/C ratio, indicative of more extensive oxidation, leads to larger d-spacing in the GO structure. It is worth noting that while the relationship is well established,

it is important to acknowledge that studies such as the one conducted by Park et al. (2022) primarily assess the spacing between atomic layers on the nanometre scale, as opposed to the overall film thickness at the micrometre scale, which is one of the of focus areas in this research.⁵⁵

The surface topography of the printed patterns of the AG films was effectively captured using profilometer technology, illustrating their consistent uniformity. The maximum and average height measurements of the thin AG films are summarised in Table 4.24. For AG 0.3, the maximum height was 0.9 μ m, with an average height of 0.7 μ m. Similarly, AG 0.4 exhibited a maximum height of 1.3 μ m and an average height of 0.9 μ m. As the concentration increased, AG 0.5 and AG 0.75 showed maximum heights of 2.4 μ m and 2.9 μ m, respectively, with average heights of 1.7 μ m and 2 μ m.

These profilometer results align well with the AFM findings presented earlier in Section 4.2, further confirming the consistency in film thickness measurements across different techniques. The increasing trend in both maximum and average heights with higher AG concentrations indicates a clear relationship between AG film thickness and concentration.

Sample	Maximum Height (μm)	Average Height(µm)
AG 0.3	0.9	0.7
AG 0.4	1.3	0.9
AG 0.5	2.4	1.7
AG 0.75	2.9	2

Table 4.24 Maximum and Average Height of Thin AG Film Samples

The height of AG films plays a significant role in providing insights into the morphology and potential properties of the material. Although AG films do not seem to exhibit a strictly layered structure like graphene, as seen in the TEM images in section 4.3.3.2, their thickness can still serve as an approximate indicator of the number of stacked particles. Furthermore, the height can have implications for the surface area, electrical conductivity, mechanical strength, and optical properties of the AG films. This information is vital for the design and fabrication of devices with specific functionalities.

4.3.3.7. SNOM and AFM

The study utilised a combined Scanning Near-Field Infrared Microscopy and Atomic Force Microscopy approach to examine the existence of Carbon-Oxygen functional groups within the AG films through vibrational spectroscopy. The AFM component effectively produced surface feature height profiles consistent with the previous observations in the section. However, the SNOM analysis did not provide conclusive evidence of the presence of Carbon-Oxygen groups.

4.3.3.8. RAMAN

Raman spectroscopy is widely used to assess the quality of graphene materials. The G-peak, occurring at approximately 1580 cm⁻¹, corresponds to the vibrational mode of sp²-bonded carbon atoms in the graphene lattice. This peak serves as a reference for monitoring changes in the graphene structure and quantifying the number of graphene layers. In rGO, the G peak is often shifted to higher frequencies compared to graphene oxide, due to the partial restoration of the sp² carbon network in the reduced material.^{56,57}

The D-peak, located around 1350 cm⁻¹, is associated with defects or disorders in the graphene lattice, activated by the breathing mode of six-membered carbon rings. The intensity of the D-peak is commonly used as an indicator of the degree of disorder within the graphene structure. Shifts in the D-peak to higher or lower frequencies can provide insights into the level of disorder or strain. ^{57,58} Additionally, the 2D peak, typically found at around 2700 cm⁻¹ in monolayer graphene, shifts to lower frequencies in bilayer and few-layer graphene due to interlayer interactions and reduced coupling.⁵⁹

As shown in Figure 4.39, the Raman spectra reveal several trends in the AG samples. D-peak intensity decreases with increasing O/C ratio, particularly in the AG 0.75 sample, where the D-peak is noticeably smaller than in AG 0.3. This trend suggests a reduction in lattice disorder with higher oxidation, which is somewhat unexpected since higher oxidation typically introduces more defects. The slight shift of the D-peak to higher frequencies with increasing O/C ratio further indicates the presence of strain within the lattice, though this shift is minimal.



Figure 4.39. Raman Spectroscopy Measurements of the AG Samples with O/C Ratio of 0.3, 0.4, 0.5 and 0.75 after Annealing. ⁴¹

The G-peak, observed around 1580 cm⁻¹, shows little to no significant shift or change in intensity across the samples with different O/C ratios. This stability in the G-peak suggests that the overall graphene structure remains largely unaffected by the oxidation process. However, the resolution along the x-axis in the Raman spectra may limit the detection of subtle shifts.

The findings, especially the unanticipated decrease in D-peak intensity as O/C ratios increase, indicate that heightened oxygen functionalization may be causing a reduction in specific structural defects. This could be attributed to a reorganisation within the graphene lattice during the oxidation process. Further examination with enhanced spectral resolution would be advantageous for validating any shifts in the 2D or G peaks and gaining a deeper understanding of these structural alterations.

4.3.4. Discussion

The section explored the characteristics of AG films with varying oxygen content (AG 0.3, AG 0.4, AG 0.5, and AG 0.75) using a range of analytical techniques. SEM analysis revealed a large-scale particulate network structure for all AG films. The TEM findings suggest the formation of multi-layer graphitic nanoparticles. The absence of substantial agglomerates suggested well-dispersed graphene sheets within the films. Pure graphene exhibited large flakes, implying a uniform structure with flat sheets, while AG films displayed larger and potentially more diverse particle sizes, likely owing to the disruption of the ordered graphene structure by oxygen functional groups. TEM analysis unveiled the intrinsic structural features of the AG films. Unlike the characteristic honeycomb lattice of pristine graphene, AG films (as seen in Fig. 4.30) showcased crumpled nanosheets at low O/C, with a gradual change to more curved structures, especially in AG 0.75, indicating the influence of oxygen content on film morphology. Interestingly, the TEM data suggested a turbostratic structure in AG films, characterised by multiple graphene layers stacked with rotational disorder. This disruption of orbital hybridisation could potentially lead to electrical conductivity similar to single-layer graphene. This finding suggests a potential advantage over single-layer graphene production, as turbostratic graphene with good conductivity can be achieved with multiple layers with a more scalable synthesis

procedure. Moreover, the observed irregularities resembled Twisted Bilayer Graphene, where layer rotation creates a Moiré superlattice and alters electrical behaviour.

Although the SNOM technique did not yield valuable data, XPS measurements confirmed the presence of oxygen in all samples, and the deconvolution of the C 1s peak provided further insight into the specific oxygen-containing functional groups present (e.g., C-OH, C=O).

The profilometry measurements have provided valuable insights into the film thickness of the AG samples, revealing a range from 0.7 μ m to 2.9 μ m. While the data does not establish a direct correlation between oxygen content and thickness, it is crucial to consider the potential structural changes induced by oxygen functionalization. The presence of oxygen-containing groups may influence the interlayer spacing within the graphene network, although this factor alone cannot account for the observed variation in thickness, which spans a factor of three. In previous studies on interlayer spacing, an increase of 10-30% was noted in interlayer distances with higher oxygen content. However, our observed thickness variation is much larger, reaching up to 300%. The films are significantly thicker than what would be expected based solely on increased interlayer spacing in stacked graphene sheets, suggesting that differences in morphology rather than simple parallel layer stacking are involved.⁵⁵ It is likely that the films are composed of 3D arrangements, potentially forming structures such as nanopores or spherical agglomerates of crumpled graphene or GO sheets. This interpretation is supported by TEM images, which show crumpled sheets, and SEM images, which depict spherical particles. These structural features are consistent with the notion that the oxygen functional groups not only disrupt the flat graphene layers but also promote the formation of complex, three-dimensional architectures, contributing to the overall increase in film thickness.

Transient absorption spectroscopy was employed to examine the excited state dynamics of the AG films. All films exhibited an initial positive $\Delta T/T$ signal across the entire measured range (420-1600 nm), attributed to the ground state absorption photobleaching. The maximum positive signal in the visible region (500-650 nm) peaked within ~65 fs. In contrast, the near-IR region displayed a strong dependence on probe wavelength with a delayed rise time, possibly due to carrier equilibration at lower energies. For all samples, the initial bleaching signal at 550 nm completely decayed, with faster decay observed for AG 0.75. A small negative $\Delta T/T$ signal around zero delay was observed for AG 0.3-0.5, particularly at 1550 nm. The decay of the positive signal showed a strong dependence on probe wavelength, with slower decay at longer wavelengths. The magnitude of the long-lived negative signal, associated with trapped electronic states, increased with the O/C ratio, suggesting a higher concentration of trapped carriers in films with higher oxygen content.

The transient absorption data presented in this chapter, as depicted in Figure 4.40, reveals several crucial processes. Before the arrival of the pump pulse, graphene initially exists in equilibrium. In Figure 4.40 (a), the photoinduced creation of narrow populations of electrons and holes leads to non-Fermi-like distributions for these charge carriers, disrupting the material's equilibrium state. Subsequently, in Figure 4.40 (b), the electrons and holes undergo carrier-carrier scattering within 10 femtoseconds, resulting in the formation of distinct Fermi-like distributions for each, with their own chemical potential but sharing the same temperature. This process signifies the rapid equilibration of the excited carrier populations.



Carrier relaxation processes in graphene

Figure 4.40. Carrier Relaxation in Graphene Under Ultrafast Light Pulses. (a) Initially, graphene is in equilibrium. When the pump arrives (depicted as a green arrow), spectrally narrow populations of electrons and holes are created, resulting in non-Fermi-like distributions for these charge carriers. (b) The electrons and holes experience carrier-carrier scattering on the 10 fs scale, forming two Fermi-like distributions. One distribution is for electrons, and the other is for holes, each with different chemical potentials but equal temperatures. (c) Auger recombination. (d) Electrons and holes recombine, and carriers relax by emitting optical phonons (as shown by dashed arrows). (e) Electron-hole recombination (yellow solid arrow representing light emission). (f) Additional cooling is facilitated by the emission of acoustic phonons (represented by a dashed arrow).⁶⁰

Figure 4.40 (c)-(e) interpret various channels through which electrons and holes recombine and thermalise within a 100-femtosecond timeframe. Figure 4.40 (c) illustrates Auger recombination, a process involving the transfer of energy from an electron-hole pair to a single electron, leading to its ejection from the material. This process is not shown in this section, but it has been observed in previous research papers. This recombination pathway is relatively infrequent in graphene compared to other semiconductors. Figure 4.40 (d) showcases electron-hole recombination with phonon emission, where electrons and holes recombine, releasing excess energy in the form of optical

phonons, serving as a significant cooling mechanism. Figure 4.40 (e) portrays electron-hole recombination, with electrons and holes directly recombining and releasing energy in the form of light, contributing to the overall reduction in the excited carrier population. Finally, Figure 4.40 (f) demonstrates additional cooling, as further cooling of the excited carriers occurs through the emission of acoustic phonons, serving as lower-energy vibrational excitations within the material compared to optical phonons.⁶⁰

Raman spectroscopy confirmed the presence of the network of sp²-bonded carbon atoms within the AG films. Further analysis of the peak positions, intensities, and their dependence on O/C would provide a more comprehensive understanding of the structure and presence of defects in the AG films.

It is evident from the XPS data that the rise in oxygen content (from AG 0.3 to AG 0.75) led to an increased concentration of oxygen-containing functional groups. This phenomenon could have influenced the thickness of the film by potentially altering the interlayer spacing. Moreover, the existence of these functional groups could have given rise to trap states, thereby affecting the optical properties and carrier dynamics of the film.

To gain a more comprehensive understanding of the impact of oxygen content on the material's properties, and because AG 0.75 displayed a broader absorption peak and slightly different data in the transient absorption spectra, it was decided to analyse additional samples. These new samples cover a complementary range of oxygen content, including both lower and higher O:C levels than AG 0.75. The following section will detail the results obtained from these additional samples.

4.4. SAMPLE SET 4: SAMPLES WITH HIGHER OXYGEN CONTENT

4.4.1. Sample Description

The fourth batch used in this research involved examining two film samples and two ink samples. The films focused on exploring the impact of oxygen content on film properties. Two new diluted aerosol films were created to better understand the distinct absorption behaviour observed in the AG 0.75 from the previous phase and determine whether 0.75 corresponds to the optimal oxygen content or if higher oxygen levels could yield even better performance. These films, printed on quartz substrates like the previous batches, were synthesised using reaction mixtures with oxygen-to-carbon (O/C) ratios of 0.6 and 0.85. However, these values refer to the O/C ratios in the reaction mixture rather than the final composition of the films. The actual oxygen content in the final samples was assessed using XPS. The unprinted inks of AG and G at their original concentrations were also analysed.

4.4.2. Characterisation Methods

This section utilised the same characterisation techniques as the previous sections, such as UV-Vis spectroscopy, pump-probe spectroscopy, and X-ray Photoelectron Spectroscopy.

4.4.3. Results

4.4.3.1. UV-VIS Results

The normalised UV-Vis spectra of AG 0.6 and AG 0.85 are compared to graphene and AG 0.75 in Figure 4.41 and Table 4.25. The spectrum of the AG 0.85 sample (pink curve) demonstrates a significant redshift, indicative of its absorption peak moving toward longer wavelengths (lower energy). This redshift is often associated with increased particle sizes or heightened structural disorder, suggesting that the AG 0.85 sample possesses larger particles, or a more disordered arrangement compared to the other samples.



Figure 4.41. The UV-Vis Absorption Spectra of AG 0.6 and AG 0.85 Compared to Graphene and AG 0.75 at Room Temperature.

In contrast, the AG 0.6 sample (green curve) exhibits two distinct absorption peaks. The first peak appears around 250 nm, with a second prominent peak near 390 nm. These two absorptions features gradually merge, forming a broader peak, which suggests the presence of distinct electronic transitions within the material. The observed differences in peak position and width likely reflect variations in particle size or film morphology, with the dual peaks of the AG 0.6 sample hinting at a more heterogeneous structure than the higher oxygen-content samples.

This spectral behaviour aligns with the morphological trends observed in Section 4.3, where films with a higher oxygen content exhibited larger particle sizes. The broader and redshifted absorption spectrum of the AG 0.85 sample is consistent with these findings, further reinforcing the correlation between oxygen content, particle size, and optical properties. As oxygen functionalisation increases, it likely induces structural changes that result in larger agglomerates or more pronounced disorders within the films, thereby shifting the absorption spectrum.

Sample	%T (800 nm)	number of layers
G	67.14	17
AG 0.6	56.83	24
AG 0.85	56.67	24

Table 4.25 Optical properties of batch 4 samples

The absorption of AG resembles that of GO, as reported in the literature.⁶¹ The peak at approximately 350-390 nm may result from electronic transitions involving the C-O bonds of the attached oxygen groups. It is difficult to pinpoint exact transitions within these groups due to broad peaks, indicating overlapping electronic transitions. These might involve different bonding orbitals or interactions within the epoxide group. The broadness could also result from a combination of C-O transitions and interactions with the π -conjugated system in AG.

4.4.3.2. Transient Absorption Spectroscopy Results

The data in Table 4.26 shows the transient absorption lifetimes measured at 550 nm for samples in batch 4, alongside reference data for G and AG 0.75 from batch 3. This data highlights trends in the decay dynamics between the batches. Notably, while samples in batch 3 required four exponential components ($\tau 1$ to $\tau 4$) for a complete description, the two samples in batch 4 could be adequately represented by three-lifetime terms, suggesting a potentially simpler decay process in batch 4 due to some variations in material properties compared to batch 3. Across both batches, all samples exhibit an ultrafast component ($\tau 1$) within the sub-picosecond regime, attributed to the initial excitation and relaxation of photogenerated carriers. Additionally, there is a growth time constant for the negative signal, possibly associated with the trapping of photoexcited carriers. A recovery component is observed in all the samples, potentially indicating the de-trapping of carriers from localised states. The presence of a long-lived component ($\tau 3$ or $\tau 4$) in all samples suggests the existence of long-lived trapped carriers. Furthermore, the lifetime analysis suggests slightly shorter lifetimes ($\tau 1$ and $\tau 2$) for samples in batch 4 compared to batch 3.

Table 4.26 Lifetimes of AG 0.6 and AG 0.85 samples from batch 4 compared to the lifetimes of graphene and AG 0.75from batch 3 at 550 nm (UV-Vis)

Kinetic lifetimes at 550 nm								
	sub-ps (ps) growth neg. signal (ps) recovery (ps) recovery						overy	
sample	τ1 (ps)	τ1 error	τ2 (ps)	τ2 error	τ3 (ps)	τ3 error	τ4 (ps)	τ4 error
G	0.114	0.003	0.643	0.092	13.530	3.509	~	0
0.6	0.023	0.009	1.201	0.115	∞	0	n/a	
0.75	0.086	0.008	0.699	n/a	1.006	n/a	~	0
0.85	0.075	0.002	1.307	0.095	∞	0	n/a	

The pre-exponential factors obtained from fitting all film samples in batches 3 and 4 offer an alternative method for comparing the magnitude of the long-lived signal relative to O/C. This signal, which does not decay, is represented by an infinite lifetime ($\tau \infty$) and an amplitude denoted A ∞ . By

comparing the ratio of A^{∞} to the initial decay lifetime amplitude (τ 1), A1, we effectively normalise the magnitude of the long-lived signal to the sample's excitation.



Figure 4.42. The Ratio of the Preexponential Factors, A∞ and A1, as a Function of O/C of the Aerosol Gel Films. O/C of the pure graphene film is defined as 0.

In Figure 4.42, we observe the variation in $A \, \varpi / A1$ as a function of O/C, with the O/C of the pure graphene film defined as 0. The consistent increase in $A \, \varpi / A1$ with increasing O/C confirms that this correlation is independent of potential fluctuations in excitation energies. However, it is essential to note that the ratio $A \, \varpi / A1$ increases as the O/C ratio rises, indicating that the relative probability of the process represented by $A \, \varpi$ becomes more dominant compared to the process described by A1 as the oxygen content rises. This suggests that higher oxygen functionalisation influences the optical transitions, potentially increasing the contribution of higher-energy electronic states (represented by $A \, \infty$ relative to the lower-energy states (represented by A1). Thus, the conclusion should be that the relative probability of the transition associated with $A \, \infty$ becomes more significant as the O/C ratio increases.

4.4.3.3. X-ray Photoelectron Spectroscopy (XPS)

The unprinted inks of AG-EC (Aerosol-Ethyl Cellulose) and G-EC (Graphene-Ethyl Cellulose) at the concentrations used during film deposition were analysed using XPS and are depicted in Figure 4.43. Both inks were dried on a flat aluminium surface before the XPS analysis. The raw, unprinted inks were not annealed and might contain surfactants. These surfactants could contribute to the peaks observed in the XPS spectra. It was observed that both inks contain Ethyl Cellulose, as indicated by the broad peak around 284-288 eV, which is characteristic of C-C bonds (the organic backbone of cellulose) and C=C bonds (in graphene-like materials). Additionally, a peak at slightly higher binding energy (around 286-287 eV) suggests C-O bonds, likely from cellulose or other oxygen-containing functional groups (such as C-OH or C-O-C) present in both inks.



Figure 4.43. XPS Analysis of C 1s Binding Energies in Graphene ink (left) and AG ink (right) with Ethyl Cellulose Surfactant.

Both inks also exhibit evidence of oxygen atoms (likely O-C or O-C-O) present in the cellulose component of both samples. XPS analysis of graphene typically shows a sharp peak around 284 eV corresponding to the C=C sp² bonding in the graphene structure. This peak is present in both inks but is much smaller in AG than in the G ink. The two largest binding energy peaks in the AG ink correspond to C-OH and C=O functional groups (although cellulose does not contain C=O, this could be C-OH or C-O-C) associated with cellulose and oxygen-containing groups in graphene. In the G ink, the C-OH component has the highest intensity compared to the C-C peak. This could be due to a larger amount of ethyl cellulose (or a smaller amount of graphene compared to ethyl cellulose).



AG Diluted Ink Films

Figure 4.44. XPS Analysis of C 1s Binding Energies in Graphene Film (left) and AG Film (right)

AG 0.6 and AG 0.85 diluted films were also analysed using XPS, as seen in Figure 4.44. AG 0.6 seems to follow the 'trend' observed in batch 3, with similar peak intensities and distributions, suggesting a consistent oxygen content and functional group presence. However, AG 0.85 appears to deviate from this trend, showing distinct differences in its XPS spectrum, most notably exhibiting almost twice the
amount of C=C bonding compared to C-C bonding. This could indicate a higher concentration of oxygen-containing groups or a different chemical environment within the film. These differences could reflect changes in the film's properties due to the increased oxygen content, which may influence its behaviour in potential applications.

4.4.4. Discussion

Analysis of the transient absorption results of the samples with high oxygen content showed that, compared to Batch 3, these films required fewer exponential components for decay analysis, potentially indicating simpler decay processes. All samples showed ultrafast carrier relaxation, a growth time constant, a recovery component, and a long-lived trapped carrier component. Batch 4 samples exhibited slightly shorter lifetimes compared to Batch 3. XPS revealed that both AG and G inks contained oxygen functionalities. The G ink displayed a sharper C=C sp2 peak compared to AG, confirming the presence of multi-layer graphene. The peak intensity distribution suggested a high concentration of oxygen groups in the G and AG inks, possibly originating from the ethyl cellulose surfactant. Similar to AG 0.75, both AG 0.6 and AG 0.85 exhibited broad optical absorption, likely due to oxygen groups and larger particle sizes. AG 0.85 displayed a redshift, while AG 0.6 had distinct absorption peaks, suggesting similarities to graphene oxide (GO).

4.5. CONCLUSION

The impact of oxygen content on the properties of multilayer graphene aerogels (AGs) in comparison to pristine multilayer graphene (G) was extensively examined in this study. The utilisation of advanced characterisation techniques such as TEM and SEM revealed significant morphological differences. Contrary to the smooth, sheet-like structure of graphene, AGs exhibited a porous and interconnected 3D network, indicative of a more complex architecture. These structural changes suggest that oxygen functionalisation not only disrupts graphene's pristine lattice but also promotes the formation of crumpled nanosheets and nanopores, potentially altering the material's properties compared to pure graphene.

Subsequent analysis via XPS confirmed the presence of oxygen-containing functional groups (C-OH, C=O, and O-C-OH) within AG annealed films, distinguishing them from pure graphene. The inclusion of these functional groups is responsible for creating defect sites and trap states, which influence the film's electronic and optoelectronic properties by altering the Fermi level and charge transport dynamics. These functional groups affect electron affinity and band structure, leading to a shift in the Fermi level that directly impacts the conductivity, carrier mobility, and overall charge concentration in the material. This tunability of electronic properties is crucial for tailoring graphene for applications such as sensors, transistors, and other optoelectronic devices.⁶²⁻⁶³

Moreover, the oxygen content in AGs has been shown to markedly influence their optical absorption characteristics, differentiating them from pristine graphene. The introduction of oxygen-containing groups within AGs is likely to generate trap states that hinder electron mobility, leading to slower recovery times in photoinduced carrier dynamics. Transient absorption spectroscopy (TAS) provided valuable insight into these ultrafast processes, revealing distinct carrier relaxation mechanisms in AGs compared to G, including the role of oxygen-induced trap states in prolonging carrier lifetimes. The pump-probe technique used in TAS allows for precise tracking of electron dynamics, enabling the study of how oxygen content modulates the relaxation timescales and energy dissipation pathways in these materials.

While pristine graphene exhibits metallic conductivity, which can limit its functionality in specific applications, the oxygen functionalisation in AGs introduces a tunable bandgap, which enhances their optoelectronic properties and responsiveness to external stimuli, such as light or chemical changes. This engineered bandgap makes AGs highly promising candidates for sensor technologies, as they provide more controlled and selective responses. The ability to customise graphene's properties through oxygen functionalisation opens up numerous possibilities for its application in next-generation electronic and sensing devices.⁶⁴

Understanding the intricate relationship between oxygen content, morphology, and optoelectronic properties in AGs is crucial for advancing their technological applications. While the current study offers valuable insights into these relationships, further theoretical modelling and experimental studies are required to explore the detailed impact of oxygen functionalisation on graphene's electronic structure and performance. The next chapter will focus on this by employing Density Functional Theory to provide a deeper theoretical analysis of oxygen-functionalised graphene's electronic and optical properties.

4.7. REFERENCES

¹ Auty, A. J., Negar Mansouriboroujeni, Nagaraja, T., Dimitri Chekulaev, Sorensen, C. M., Das, S. R., Martsinovich, N., & Adrien. (2022). Ultrafast Transient Absorption Spectroscopy of Inkjet-Printed Graphene and Aerosol Gel Graphene Films: Effect of Oxygen and Morphology on Carrier Relaxation Dynamics. *The Journal of Physical Chemistry C*, *126*(18), 7949–7955. https://doi.org/10.1021/acs.jpcc.2c01086

² Das, Nagaraja, Krishnamoorthy, US Patent Disclosure 2022-044 (Kansas State University)

³ Nagaraja, T., Krishnamoorthy, R., Asif, M., Lacroix, B., & Das, S. R. (2023). Microplotter-Printed Graphene-Based Electrochemical Sensor for Detecting Phosphates. *ACS Applied Nano Materials*, *6*(21), 20288–20297. <u>https://doi.org/10.1021/acsanm.3c04228</u>

⁴ Anand, Xiang, W., Arjun Nepal, Wright, J. P., Chen, P., Nagaraja, T., Shusil Sigdel, LaCroix, B., Sorensen, C. M., & Das, S. R. (2021). Graphene Aerosol Gel Ink for Printing Micro-Supercapacitors. *ACS Applied Energy Materials*, *4*(8), 7632–7641. <u>https://doi.org/10.1021/acsaem.1c00919</u>

⁵ XPS performed by Dr Debora Hammond at the University of Sheffield

⁶ SEM performed at Kansas State University

⁷ Apparatus in the Chemistry department of the University of Sheffield (UV-Vis)

⁸ Lord Porter Laser Lab at the University of Sheffield (Helois)

⁹ Origin Pro versions 2019 and 2023b: Origin and OriginPro - Data Analysis and Graphing Software. (n.d.). Www.originlab.com. <u>https://www.originlab.com/</u>

¹⁰ Surface Xplorerversion 4.2: Data Analysis Software by Ultrafast Systems. (2024). Ultrafast Systems. <u>https://www.ultrafast.systems/products/spectrometers-accessories/surface-xplorer/</u>

¹¹ AFM apparatus at the University of Sheffield

¹² Gwyddion software version 2.62: Gwyddion – Free SPM (AFM, SNOM/NSOM, STM, MFM, ...) data analysis software. (2025). Gwyddion.net. <u>https://gwyddion.net/</u>

¹³ Gengler, R. Y. N., Badali, D. S., Zhang, D., Dimos, K., Spyrou, K., Gournis, D., & Miller, R. J. D. (2013). Revealing the ultrafast process behind the photoreduction of graphene oxide. *Nature Communications*, *4*(1). <u>https://doi.org/10.1038/ncomms3560</u>

¹⁴ Lai, Q., Zhu, S., Luo, X., Zou, M., & Huang, S. (2012). Ultraviolet-visible spectroscopy of graphene oxides. *AIP Advances*, 2(3), 032146. <u>https://doi.org/10.1063/1.4747817</u>

¹⁵ Nair, R. R., Blake, P., Grigorenko, A. N., Novoselov, K. S., Booth, T. J., Stauber, T., Peres, N. M. R., & Geim, A. K. (2008). Fine Structure Constant Defines Visual Transparency of Graphene. *Science*, *320*(5881), 1308–1308. https://doi.org/10.1126/science.1156965

¹⁶ Li, W., Chen, B., Meng, C., Fang, W., Xiao, Y., Li, X., Hu, Z., Xu, Y., Tong, L., Wang, H., Liu, W.-T., Bao, J., & Shen, Y. R. (2014). *Ultrafast All-Optical Graphene Modulator*. *14*(2), 955–959. <u>https://doi.org/10.1021/nl404356t</u>

¹⁷ R. Somphonsane, Ramamoorthy, H., G. Bohra, He, G., Ferry, D. K., Ochiai, Y., Aoki, N., & Bird, J. P. (2013). Fast Energy Relaxation of Hot Carriers Near the Dirac Point of Graphene. *Nano Letters*, *13*(9), 4305–4310. <u>https://doi.org/10.1021/nl4020777</u>

¹⁸ Newson, R. W., Dean, J., Schmidt, B., & van Driel, H. M. (2009). Ultrafast carrier kinetics in exfoliated graphene and thin graphite films. *Optics Express*, *17*(4), 2326. <u>https://doi.org/10.1364/oe.17.002326</u>

¹⁹ Shang, J., Luo, Z., Cong, C., Lin, J., Yu, T., & Gurzadyan, G. G. (2010). Femtosecond UV-pump/visible-probe measurements of carrier dynamics in stacked graphene films. *Applied Physics Letters*, *97*(16), 163103. https://doi.org/10.1063/1.3504704

²⁰ Dawlaty, J. M., Shriram Shivaraman, Mvs Chandrashekhar, Rana, F., & Spencer, M. G. (2008). Measurement of ultrafast carrier dynamics in epitaxial graphene. *Applied Physics Letters*, *92*(4). https://doi.org/10.1063/1.2837539

²¹ Sun, D., Wu, Z.-K., Divin, C., Li, X., Berger, C., de Heer, W. A., First, P. N., & Norris, T. B. (2008). Ultrafast Relaxation of Excited Dirac Fermions in Epitaxial Graphene Using Optical Differential Transmission Spectroscopy. *Physical Review Letters*, *101*(15). <u>https://doi.org/10.1103/physrevlett.101.157402</u>

²² Massicotte, M., Giancarlo Soavi, Principi, A., & Klaas-Jan Tielrooij. (2021). Hot carriers in graphene – fundamentals and applications. *Nanoscale*. <u>https://doi.org/10.1039/d0nr09166a</u>

²³ Kaniyankandy, S., Achary, S. N., Rawalekar, S., & Ghosh, H. N. (2011). Ultrafast Relaxation Dynamics in Graphene Oxide: Evidence of Electron Trapping. *The Journal of Physical Chemistry C*, *115*(39), 19110–19116. https://doi.org/10.1021/jp206923q

²⁴ Huang, L., Hartland, G. V., Chu, L.-Q., Luxmi, Feenstra, R. M., Lian, C., Tahy, K., & Xing, H. (2010). Ultrafast Transient Absorption Microscopy Studies of Carrier Dynamics in Epitaxial Graphene. *Nano Letters*, *10*(4), 1308– 1313. <u>https://doi.org/10.1021/nl904106t</u>

²⁵ Tang, X., Debliquy, M., Lahem, D., Yan, Y., & Raskin, J.-P. (2021). A Review on Functionalized Graphene Sensors for Detection of Ammonia. *Sensors*, *21*(4), 1443. <u>https://doi.org/10.3390/s21041443</u>

²⁶ Wang, T., Huang, D., Yang, Z., Xu, S., He, G., Li, X., Hu, N., Yin, G., He, D., & Zhang, L. (2015). A Review on Graphene-Based Gas/Vapor Sensors with Unique Properties and Potential Applications. *Nano-Micro Letters*, 8(2), 95–119. <u>https://doi.org/10.1007/s40820-015-0073-1</u>

²⁷ Pasanen, H. P., Khan, R., Odutola, J. A., & Tkachenko, N. V. (2024). Transient Absorption Spectroscopy of Films: Impact of Refractive Index. The Journal of Physical Chemistry C, 128(15), 6167–6179. https://doi.org/10.1021/acs.jpcc.4c00981

²⁸ FTIR and ATR were performed at the Chemistry department of the University of Sheffield

²⁹ LibreTexts. (2014, November 30). *Infrared Spectroscopy Absorption Table*. Chemistry LibreTexts. <u>https://chem.libretexts.org/Ancillary Materials/Reference/Reference Tables/Spectroscopic Reference Table</u> <u>s/Infrared_Spectroscopy_Absorption_Table</u>

³⁰ Rai, V. N., Jain, B., Mukherjee, C., Choudhary, P., Saxena, P., & Mishra, A. (2020). Study of degradation behavior in Kapton foil after gamma irradiation at low fluence. *Radiation Effects and Defects in Solids*, *175*(9-10), 879– 891. <u>https://doi.org/10.1080/10420150.2020.1780593</u>

³¹ Ethyl cellulose | 9004-57-3. (2024). ChemicalBook. https://www.chemicalbook.com/ChemicalProductProperty_EN_CB6165620.htm

³² *alpha-Terpineol*. (2025). TCIchemicals.com. <u>https://www.tcichemicals.com/GB/en/p/T0022</u>

³³ ChemDraw - Revvity Signals Software. (n.d.). Revvitysignals.com. https://revvitysignals.com/products/research/chemdraw

³⁴ Çiplak, Z., Yildiz, N., & Çalimli, A. (2014). Investigation of Graphene/Ag Nanocomposites Synthesis Parameters for Two Different Synthesis Methods. *Fullerenes, Nanotubes and Carbon Nanostructures, 23*(4), 361–370. https://doi.org/10.1080/1536383x.2014.894025 ³⁵ Cançado, L. G., Jorio, A., Ferreira, E. H. M., Stavale, F., Achete, C. A., Capaz, R. B., Moutinho, M. V. O., Lombardo, A., Kulmala, T. S., & Ferrari, A. C. (2011). Quantifying Defects in Graphene via Raman Spectroscopy at Different Excitation Energies. *Nano Letters*, *11*(8), 3190–3196. <u>https://doi.org/10.1021/nl201432g</u>

³⁶ Krishna, D. N. G., & Philip, J. (2022). Review on surface-characterization applications of X-ray photoelectron spectroscopy (XPS): Recent developments and challenges. *Applied Surface Science Advances*, *12*, 100332. https://doi.org/10.1016/j.apsadv.2022.100332

³⁷ Datt Bhatt, M., Kim, H., & Kim, G. (2022). Various defects in graphene: a review. *RSC Advances*, *12*(33), 21520–21547. <u>https://doi.org/10.1039/D2RA01436J</u>

³⁸ TEM performed with the assistance of John Nutter at Henry Royce Institute (TUOS).

³⁹ Profilometer at the Henry Royce Institute at the University of Sheffield, Department of Materials.

⁴⁰ SNOM was performed at the department of Physics by the guidance of Dr. Alex Knight, at the University of Sheffield

⁴¹ Raman spectroscopy performed by Thiba Nagaraja at Kansas State University

⁴² Hummers, W. S., & Offeman, R. E. (1958). Preparation of Graphitic Oxide. *Journal of the American Chemical Society*, *80*(6), 1339–1339. <u>https://doi.org/10.1021/ja01539a017</u>

⁴³ Ibrahim, A., Klopocinska, A., Horvat, K., & Abdel Hamid, Z. (2021). Graphene-Based Nanocomposites: Synthesis, Mechanical Properties, and Characterizations. *Polymers*, *13*(17), 2869. <u>https://doi.org/10.3390/polym13172869</u>

⁴⁴ Eberlein, T., Bangert, U., Nair, R. R., Jones, R., Gass, M., Bleloch, A. L., Novoselov, K. S., Geim, A., & Briddon, P. R. (2008). Plasmon spectroscopy of free-standing graphene films. *Physical Review B*, 77(23). https://doi.org/10.1103/physrevb.77.233406

⁴⁵ Phurida Kokmat, Piyaporn Surinlert, & Akkawat Ruammaitree. (2023). Growth of High-Purity and High-Quality Turbostratic Graphene with Different Interlayer Spacings. *ACS Omega*, *8*(4), 4010–4018. <u>https://doi.org/10.1021/acsomega.2c06834</u>

⁴⁶ Kim, K., Yankowitz, M., Fallahazad, B., Kang, S., Movva, H. C. P., Huang, S., Larentis, S., Corbet, C. M., Taniguchi, T., Watanabe, K., Banerjee, S. K., LeRoy, B. J., & Tutuc, E. (2016). van der Waals Heterostructures with High Accuracy Rotational Alignment. *Nano Letters*, *16*(3), 1989–1995. https://doi.org/10.1021/acs.nanolett.5b05263

⁴⁷ Mai, P., Huang, E. W., Yu, J., Feldman, B. E., & Phillips, P. W. (2022). Interaction-driven Spontaneous Ferromagnetic Insulating States with Odd Chern Numbers. *ArXiv (Cornell University)*. <u>https://doi.org/10.48550/arxiv.2205.08545</u>

⁴⁸ Wang, J., Ma, F., Liang, W., & Sun, M. (2017). Electrical properties and applications of graphene, hexagonal boron nitride (h-BN), and graphene/h-BN heterostructures. *Materials Today Physics*, *2*, 6–34. <u>https://doi.org/10.1016/j.mtphys.2017.07.001</u>

⁴⁹ Cao, Y., Fatemi, V., Fang, S., Watanabe, K., Taniguchi, T., Kaxiras, E., & Jarillo-Herrero, P. (2018). Unconventional superconductivity in magic-angle graphene superlattices. *Nature*, *556*(7699), 43–50. <u>https://doi.org/10.1038/nature26160</u>

⁵⁰ Wang, J., Mu, X., & Sun, M. (2019). The Thermal, Electrical and Thermoelectric Properties of Graphene Nanomaterials. *Nanomaterials*, *9*(2), 218. <u>https://doi.org/10.3390/nano9020218</u>

⁵¹ Makuła, P., Pacia, M., & Macyk, W. (2018). How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *The Journal of Physical Chemistry Letters*, *9*(23), 6814–6817. <u>https://doi.org/10.1021/acs.jpclett.8b02892</u>

⁵² Carbon | XPS Periodic Table | Thermo Fisher Scientific - UK. (2023). Thermofisher.com. https://www.thermofisher.com/uk/en/home/materials-science/learning-center/periodic-table/nonmetal/carbon.html

⁵³ Shearer, C. J., Slattery, A. D., Stapleton, A. J., Shapter, J. G., & Gibson, C. T. (2016). Accurate thickness measurement of graphene. *Nanotechnology*, *27*(12), 125704. <u>https://doi.org/10.1088/0957-4484/27/12/125704</u>

⁵⁴ Zhang, H., Chen, C., Zhao, W., Li, Z., Kou, L., Zhang, Z., & Stiens, J. (2023). Effect of graphene film thickness on photoluminescence properties of ZnO/graphene composite films. *Ceramics International*, *49*(18), 30864–30874. https://doi.org/10.1016/j.ceramint.2023.07.044

⁵⁵ Park, J., Lee, W., Nam, J., Joong Tark Han, Choi, C.-J., & Jun Yeon Hwang. (2022). A study of the correlation between the oxidation degree and thickness of graphene oxides. Carbon, 189, 579–585. https://doi.org/10.1016/j.carbon.2021.12.101

⁵⁶ Ben Gouider Trabelsi, A., V. Kusmartsev, F., Kusmartseva, A., H. Alkallas, F., AlFaify, S., & Shkir, M. (2020). Raman Spectroscopy Imaging of Exceptional Electronic Properties in Epitaxial Graphene Grown on SiC. *Nanomaterials*, *10*(11), 2234. https://doi.org/10.3390/nano10112234

⁵⁷ Syed Muhammad Hafiz, Ritikos, R., Whitcher, T., Nadia Md. Razib, Daniel, Narong Chanlek, Nakajima, H., Thanit Saisopa, Prayoon Songsiriritthigul, Huang, N. M., & Saadah Abdul Rahman. (2014). A practical carbon dioxide gas sensor using room-temperature hydrogen plasma reduced graphene oxide. *Sensors and Actuators B-Chemical*, *193*, 692–700. <u>https://doi.org/10.1016/j.snb.2013.12.017</u>

⁵⁸ Ferrari, A. C. (2007). Raman spectroscopy of graphene and graphite: Disorder, electron–phonon coupling, doping and nonadiabatic effects. *Solid State Communications*, *143*(1), 47–57. https://doi.org/10.1016/j.ssc.2007.03.052

⁵⁹ Malard, L. M., Pimenta, M. A., Dresselhaus, G., & Dresselhaus, M. S. (2009). Raman spectroscopy in graphene. *Physics Reports*, 473(5-6), 51–87. <u>https://doi.org/10.1016/j.physrep.2009.02.003</u>

⁶⁰ Diogo, Dias, R., Manuel, & Vasilevskiy, M. I. (2024). Two-Step Relaxation of Non-Equilibrium Electrons in Graphene: The Key to Understanding Pump–Probe Experiments. *Applied Sciences*, *14*(3), 1250–1250. https://doi.org/10.3390/app14031250

⁶¹ Wijaya, R., Andersan, G., Permatasari Santoso, S., & Irawaty, W. (2020). Green Reduction of Graphene Oxide using Kaffir Lime Peel Extract (Citrus hystrix) and Its Application as Adsorbent for Methylene Blue. *Scientific Reports*, *10*(1). <u>https://doi.org/10.1038/s41598-020-57433-9</u>

⁶² Çiplak, Z., Yildiz, N., & Çalimli, A. (2014). Investigation of Graphene/Ag Nanocomposites Synthesis Parameters for Two Different Synthesis Methods. *Fullerenes, Nanotubes and Carbon Nanostructures, 23*(4), 361–370. <u>https://doi.org/10.1080/1536383x.2014.894025</u>

⁶³ Hunt, A., E.Z. Kurmaev, & A. Moewes. (2014). Band gap engineering of graphene oxide by chemical modification. *Carbon*, *75*, 366–371. <u>https://doi.org/10.1016/j.carbon.2014.04.015</u>

⁶⁴ Warner, J. H., Schaffel, F., Rummeli, M., & Alicja Bachmatiuk. (2013). *Graphene : fundamentals to applications*. Kidlington, Oxford: Elsevier.

5. Computational Modelling of Graphene-Based Materials

CONTENTS

List of Figures	
List of Tables	
Overview	
5.1. Computational Methodology	
5.1.1. Geometry Optimisation	
5.1.2. Optical Calculations	
5.1.3. Density of States and Projected Density of States Calculations	
5.1.4. Band Structure Calculations	
5.2. Background: Electronic Properties of Pure Graphene	
5.2.1. Electronic Structure (Density of Sates) of Pure Graphene	
5.2.2. Band Structures of Pure Graphene	
5.2.3. Optical Calculations of Pure Graphene	
5.2.4. Motivation: from graphene to functionalised graphene	
5.3. Graphene with Oxygen Groups	
5.3.1. Graphene with Epoxides and Annulene Groups	
5.3.1.1. Electronic Structure	
5.3.1.2. Band Structures and Band Gap Opening	
5.3.1.3. Optical Properties of Epoxide-Containing Graphene	
5.3.2 Graphene Nanoribbons (GNRs)	
5.3.2.1. Electronic structure	
5.3.2.2. Optical Absorption	201
5.3.3. Graphene with Hydroxyl Groups	202
5.3.3.1. Electronic Structures and Band Structures	205
5.3.3.2. Optical Absorption	207
5.3.4. Oxygen Substitution	
5.3.4.1. Electronic Structure	
5.3.5. Discussion	212
5.4.The effects of curvature on Graphene	214
5.4.1. Graphene with Curvature	214
5.4.1.1. Electronic structure	215
5.4.1.2. Optical Properties	216
5.4.2. Curved graphene with oxygen groups	217
5.4.2.1. Electronic Properties	218
5.4.2.2. Optical Properties	220
5.4.3. Discussion	

5.5. Graphene with a Monovacancy and Other Defects	222
5.5.1. Monovacancy Defect and Oxygen Groups	222
5.5.1.1. Electronic Properties	223
5.5.1.2. Optical Properties	225
5.5.2. Stone-Wales (SW) Defects with Oxygen Groups	226
5.5.2.1. Electronic Properties	227
5.5.2.2. Optical Properties	228
5.5.3. Discussion	229
5.6. Conclusion	231
5.7. References	232

LIST OF FIGURES

Figure 5.1. (a) Density of Electronic States of Pure Graphene, (b) Band Structure of Pure Graphene, and (c) Calculated Absorption Spectrum of Pure Graphene.

Figure 5.2. Showing the Epoxide's Triangular Ring (oxygen-carbon-carbon) Bonds to Graphene's Carbon Lattice. Bond lengths: C-O = 1.461 Å, C-O = 1.461 Å, and C-C beneath O = 1.50 Å after optimization. The C-O-C bond angle is also depicted.

Figure 5.3. Graphene Supercells with Various Arrangements of Epoxide Groups and Annulene Groups. Most stable structures are marked with a red box.

Figure 5.4. Curvature Induced by Epoxidation. Following Geometry Optimisation, Graphene Structures with Epoxide Groups Exhibit Slight Curvatures, Deviating from their Initial Flat Geometry.

Figure 5.5. Graphs Depicting the Density of States of 424 Graphene with Epoxide Groups Compared to Pure Graphene. (a) DOS Graphs of Graphene with an Increasing Number of Epoxide Groups, with the Projected DOS of Oxygen Atoms Shown in Red. (b) DOS Graphs of All Structures with two Epoxide Groups. (c) DOS of Selected Structures with Two Epoxide Groups, where the Contribution of Oxygen Atoms are Shown in Red.

Figure 5.6. Projected DOS Graphs of Carbon Atoms Around the Epoxide Groups for Structure Named 1,4 (20).

Figure 5.7. Projected DOS Graphs of Carbon Atoms Close and Far from the Epoxide Group in a 8¹/₂8 Graphene Unit Cell with One Epoxide Group.

Figure 5.8. Band Structures of Graphene with Different Arrangements of Epoxide Groups

Figure 5.9. Calculated Absorbance of (a) Graphene (G) with an Increasing Number of Epoxide groups, (b) all Graphene Structures with Two Epoxide Groups, (c) Graphene with Three Epoxide Groups, and (d) Graphene with Four Oxygen Groups, All Data Cropped from 200 nm to 800 nm to Match the Experimental Range.

Figure 5.10. Graphene Nanoribbons Created by the Presence of Epoxide and Annulene Groups.

Figure 5.11. Graphs of the DOS of GNR with a Chain of Epoxides (left) and Zigzag (right) GNRs, with the PDOS of Oxygen Shown in Red.

Figure 5.12. Calculated Band Structures of GNR with a chain of Epoxides (left) and Zigzag (right) GNR with annulene groups.

Figure 5.13. Calculated Optical Absorption Spectra of GNRs Functionalised with Epoxide and Annulene Groups, Compared to Pure Graphene.

Figure 5.14. 4by4 Graphene Supercell with Various Arrangements of OH Groups.

Figure 5.15. DOS of Pure Graphene (black like), Graphene with 2 OH Groups (in blue) and 4 OH Groups (in green), with the PDOS of Oxygen Shown in Red.

Figure 5.16. Calculated Band Structures of Four Selected Graphene Structures with Two or Four OH Groups

Figure 5.17. Calculated Optical Absorption Spectra of Pure Graphene and Graphene with OH Groups.

Figure 5.18. Optimised Atomic Structures of Graphene with One, Two and Three Oxygen Substitutions.

Figure 5.19. Left: Density of States Graphs Comparing Pristine Graphene (Black) and Graphene with an Increasing Number of Substituted Oxygens. Right: Optical Absorbance Graphs of the Same Structures.

Figure 5.20. Top row: Calculated band structures for graphene with 1 substitutional oxygen atom (left), 2 substitutional oxygen atoms (centre) and 3 substitutional oxygen atoms (right). Bottom row: Optimised atomic structures corresponding to the graphs in the top row.

Figure 5.21. Calculated Optical Absorbance of Graphene with Substituted Oxygen Compared to Pure Graphene

Figure 5.22. Relative energies of zigzag (red) and armchair (blue) graphene structures as a function of lattice compression percentage. Representative structural models of the compressed graphene sheets are shown.

Figure 5.23. Density of States for Zigzag and Armchair Curved Graphene Structures.

Figure 5.24. Band structures of zigzag (left) and armchair (right) curved graphene models at 20% compression.

Figure 5.25. Optical Absorption Spectra of Curved Graphene

Figure 5.26. 6by6 Graphene with Curvatures with Oxygen Groups.

Figure 5.27. The Total and Projected Oxygen (O) Density of States for Curved Zigzag and Armchair Graphene Structures.

Figure 5.28. The Band Structures of the Z80+1 O Sub (left) and A80+1 Epoxide (right) Systems. A Dashed Red Line Indicates the Fermi Level.

Figure 5.29. Panel (a) Compares Pristine Graphene, Zigzag Curved Graphene Z80, and Z80 with a Single Substitutional Oxygen Atom (Z80 + 1 O Sub). Panel (b) Compares Pristine Graphene, Armchair Curved Graphene A80, and A80 with a Single Epoxide Group (A80 + 1 epoxide). The spectra were cropped in the wavelength range of 200-800 nm.

Figure 5.30. Graphene structures with Different Types of Defects: (a) Monovacancy, (b) Monovacancy and Oxygen Substitution, (c) Monovacancy and Two OH Groups.

Figure 5.31. DOS of Pristine Graphene Compared with the DOS Of Graphene with a Monovacancy (1 Vacancy), Graphene with Monovacancy and a Substitutional Oxygen Atom (1 V + 1 O Sub), and Graphene with a Monovacancy and Two Hydroxyl Groups (1 V + 2 OH). The red line shows the PDOS of oxygen.

Figure 5.32. Band Structures of (left) Graphene with a Single Vacancy, (middle) Graphene with a Vacancy and a Substitutional Oxygen Atom, and (right) Graphene with a Vacancy and Two Hydroxyl Groups.

LIST OF TABLES

Table 5.1 Table including relative energies of 4by4 graphene structures with epoxide functional groups compared to graphene, table includes total and fermi energies (eV)

 Table 5.2 Calculated band gap values for graphene 4by4 with epoxide groups.

Table 5.3 Bandgap and total energy values for Oxygen containing GNRs.

Table 5.4 Table including relative energies of 4by4 graphene structures with OH functional groups compared to graphene, table includes total and fermi energies (eV)

Table 5.5 Table of the calculated energies of graphene with substituted oxygen

 Table 5.6 Calculated total and fermi energies of curved graphene structures

Table 5.7 Relative Energies of Curved Graphene Structures with Oxygen Groups

Table 5.8 Electronic Properties of Graphene Structures with Vacancies and Oxygen Functionalisation.

Table 5.9 Comparative Energetics of Epoxide-Functionalised Graphene and SW-Defected Graphene

Computational Modelling of Graphene-Based Materials

OVERVIEW

This chapter reports our quantum chemistry investigations of the structure-property relationship of a series of graphene-based materials to find out how morphological and chemical modifications affect graphene's electronic and optical properties. The materials explored include:

- Pure graphene;
- graphene derivatives functionalised with different types of oxygen groups at varying concentrations and configurations;
- curved graphene with different curvatures;
- graphene with substitutional oxygen defects.

5.1. COMPUTATIONAL METHODOLOGY

Density functional theory calculations were performed using the SIESTA software package. To model weak interactions between atoms accurately, the van der Waals (VDW) functional vdW-DF2 by Lee et al. was employed to describe exchange-correlation.¹

The calculations used norm-conserving pseudopotentials, which simplify calculations by replacing core electrons with an effective potential. These pseudopotentials were used in combination with double-zeta polarised basis sets for valence electrons. Pseudopotentials optimised using the GGA-PBE (Generalized Gradient Approximation, and the exchange-correlation functional of Perdew, Burke, and Ernzerhof)² approximation and the basis sets optimised specifically for these pseudopotentials were obtained from Simune Atomistic database.^{3,4}

The simulation systems were periodic in two dimensions, with a vacuum thickness of 30 to 40 Å (depending on the system) in the third dimension. A Monkhorst-Pack k-point grid of 24x24x1 was used for geometry optimisation for the graphene structures.

5.1.1. Geometry Optimisation

Geometry optimisation employed the Conjugate Gradient (CG) algorithm. This minimisation technique iteratively refines the atomic positions to locate a local minimum on the potential energy surface. To prevent excessively large atomic movements that could destabilise the simulation, a maximum atomic displacement of 0.1 Angstrom per step was imposed. The convergence criterion for the optimisation was based on the magnitude of the forces acting on each atom. The calculations stopped when the maximum force fell below a 0.01 eV/Angstrom threshold. All atoms were allowed to be optimised, while the lattice parameters of the simulation cell were fixed during the optimisation process. An example of the input file is provided in the appendix for reference.

5.1.2. Optical Calculations

In the investigation, the optical properties were explored, enabling the calculation of the absorption spectra within the SIESTA framework. SIESTA's simulation of optical properties is based on calculating the imaginary part of the dielectric function by computing dipolar transition matrix elements for transitions between occupied and unoccupied orbitals obtained in ground state calculations.

Several key parameters, including the number of bands, the energy range, the broadening and the number of k points, were used to control optical calculations in SIESTA.

The number of bands determines the electronic states included in the calculation, impacting both the accuracy and computational cost. Tests were conducted with a limited number of bands as well as with all available bands. As increasing the number of bands did not notably extend the computational time, it was decided to incorporate all available bands to enhance accuracy.

The k-point mesh plays a crucial role in accurately integrating electronic properties over the Brillouin zone. Different densities of the k-point grid were tested. The k-point grid size was tested for a model two-atom graphene unit cell. The k-point grid size was varied from a coarse grid of 6x6x1 to a very fine grid of 192x192x1. This investigation revealed that a k-point grid size of at least 96x96x1 was necessary to achieve fully converged spectra. However, a balance between accuracy and computational efficiency is crucial. Considering this, a k-point grid of 24x24x1 was determined to be a good compromise. This grid size provided a reasonable level of accuracy while being significantly faster to compute compared to the very fine grid. In some cases, an even coarser grid of 12x12x1 was used when computational efficiency was a top priority.

The minimum and maximum energies specify the energy range of interest. In the study, the calculations were performed within a range of 0.0 Ry to 2.0 Ry. To account for the inherent broadening of spectral features due to various factors like electron-phonon coupling and finite lifetime of excited

states, a line broadening factor of 0.2 eV was incorporated, which broadened the calculated absorption peaks, making them more comparable to experimental observations.

An analysis tool provided by the SIESTA distribution, called 'optical.f', file was used to process the imaginary part of the dielectric function calculated by SIESTA. This post-processing produced a file called 'absorp_coef.out', which contained values of the absorption coefficient as a function of energy (eV). For plotting the spectra, the values of energy were converted into wavelength using equation (5.1).

$$\lambda (nm) = \frac{1240}{E (eV)}$$
(5.1)

The calculated data provide absorbance values in the range from 0 nm to 6000 nm—8000 nm, depending on the system. To match the experimentally accessible range of frequencies, calculated spectra were plotted in the range 200 nm to 800 nm.

5.1.3. Density of States and Projected Density of States Calculations

To gain a comprehensive understanding of the properties of graphene-based materials, the research explored the electronic structure of the materials, extending beyond their optical properties. Calculations were performed to determine the density of states (DOS) and the projected or partial density of states (PDOS) of graphene and graphene-based materials. The DOS provides a comprehensive picture of the available electronic states for a material at a specific energy range. It gives information on the distribution of electronic energy states within the material. The PDOS decomposes the total DOS further, allowing for analysis of the contribution of individual atoms or specific elements to the overall DOS. This detailed information provides valuable insights into the electronic properties of materials.

DOS calculations were done in the energy range from -20 to 20 eV (where zero is the energy of electron in vacuum). This energy range was discretised by taking 2000 points in this energy window. Furthermore, a broadening of 0.100 eV was applied to the peaks obtained from calculations of DOS. This broadening factor accounts for the finite lifetime of electronic states and serves to smooth out the DOS spectrum for better visualisation. The Fmdos.f analysis tool, provided by the SIESTA distribution, was utilised to post-process the calculated PDOS data.

5.1.4. Band Structure Calculations

The band structure refers to the allowed energy levels for electrons within a material as a function of k-points in the Brillouin zone, visualised as bands separated by energy gaps. In this study, band structure calculations were performed to determine the energy dispersion of electrons throughout the Brillouin zone, which is the unit cell in the reciprocal lattice of the material. An appropriate k-point path ensures accurate sampling of the Brillouin zone and a reliable representation of the band structure.

For these calculations, a series of k-points were specified along specific high-symmetry directions within the Brillouin zone of graphene. These k-points acted as waypoints for calculating the electronic band energies. Each k-point was specified by its coordinates relative to the reciprocal lattice vectors. Labels were used to specify these k-points as high-symmetry points (Γ , P, S, and Y). An analysis tool called 'gnubands.f' supplied within the SIESTA distribution was used to analyse the calculated band structure data.

5.2. BACKGROUND: ELECTRONIC PROPERTIES OF PURE GRAPHENE

5.2.1. Electronic Structure (Density of Sates) of Pure Graphene

The DOS refers to the number of electronic states available per unit of energy and per unit cell in the material. Unlike conventional semiconductors, pure graphene lacks a band gap separating valence and conduction bands. Rather, it exhibits a zero band gap at specific points in its Brillouin zone, called Dirac points (K and K'), implying that there is no significant energy barrier for electrons to transition between the valence and conduction bands. In the vicinity of these points, the DOS has a linear relationship with energy, indicating high mobility of electrons and holes. This contributes to graphene's high conductivity, as electrons readily occupy the conduction band and facilitate efficient current flow. In agreement with previous theoretical studies⁵, our calculations demonstrate a zero band gap of graphene, as illustrated in the graphical representation of the calculated DOS of graphene in Figure 5.1 (a).



Figure 5.1. (a) Density of Electronic States of Pure Graphene, (b) Band Structure of Pure Graphene, and (c) Calculated Absorption Spectrum of Pure Graphene. All Properties Were Calculated in a 4 × 4 Rectangular Graphene Unit Cell. In All Density of States Plots, Zero Energy Corresponds to the Fermi level. In All Band Structure Plots, Zero Energy Corresponds to the Vacuum Level, and the Fermi Level Is Shown with a Dashed Red Line.

5.2.2. Band Structures of Pure Graphene

The exceptional band structure of graphene has been subject to extensive study. In 1947, P.R. Wallace conducted the first theoretical study of the band structure of graphene and predicted its semi-metallic behaviour.⁶ Later in the 1960s, Linus Pauling proposed graphene as a resonant valence bond (RVB) structure, suggesting strong electron-electron interactions in graphene, similar to transition elements, which contrasts with the band theory view.⁷ The Slonczewski-Weiss-McClure (SWM) band structure model was later successful in describing the electronic properties of graphite and graphene for many years.^{8,9}

In conventional semiconductors, electrons are confined to specific energy bands determined by the crystal lattice's periodic potential. However, in graphene, the valence and conduction bands converge at specific points in the momentum space, known as Dirac points. Most experimental data supports the band structure model of graphene as a semimetal with distinctive low-energy electron excitations known as Dirac fermions. These fermions act as massless particles akin to those in quantum electrodynamics (QED) but with much lower velocities.⁵

The band structure of pure graphene, as calculated in this work, is presented in Figure 5.1 (b). This band structure has been widely documented in literature.^{8,10,11} Graphene and other materials that do not have a band gap display a distinct band structure in which the valence and conduction bands either intersect or have minimal separation at specific points in momentum space. In essence, the absence of a substantial band gap imparts metallic-like characteristics to these materials. This manifests as

electrical properties resembling those of metals, a consequence of the ease with which electrons can be excited and conduct electricity.¹²

5.2.3. Optical Calculations of Pure Graphene

The study presented in Chapter 4 measured the UV-Vis absorption spectra of graphene. These spectra exhibit a distinct peak at approximately 276 nm, in good agreement with the theoretical data presented in Figure 5.1 (c). This close agreement between experimental and theoretical results provides strong validation for the employed computational methods. Theoretical calculations anticipate a narrow absorption peak in the near-UV region, with a maximum at approximately 295 nm. Conversely, experimental measurements indicated a slightly shorter wavelength of about 276 nm in the UV region, with a broader peak. The calculated absorption peak illustrated in Figure 5.1 (c) for the pure graphene model corresponds to approximately 4.2 eV; comparable experimental results have demonstrated that a single-layer graphene sheet can yield a similar spectrum with the maximum at the energy value of 4.6 eV.¹³ This study's experimental part (Chapter 4), analysing graphene films with approximately 7 layers, similarly yielded a maximum absorption peak of around 4.6 eV.

The delocalised nature of the π electrons in graphene makes light absorption different from finite systems, such as benzene and polyaromatic hydrocarbons. Graphene's π electrons are not confined to individual bonds but are spread across the entire graphene sheet. This delocalisation results in energy bands and allows graphene to absorb a wide range of photon energies, resulting in broad, weak absorption instead of a sharp peak typical of a π to π^* transition in a single molecule. Therefore, pure single-layer graphene has very weak broad absorption in the UV-VIS region.

5.2.4. Motivation: from graphene to functionalised graphene.

The properties of graphene depend on various factors, including its structure, functionalisation, and defects. Building upon the experimental findings presented in Chapter 4, a theoretical investigation was conducted to gain a deeper understanding of experimentally obtained aerogel graphene films. The investigation explored how introducing oxygen groups, curvature, and other defects within the graphene lattice can influence these properties, in order to gain a deeper understanding of the structure, functionality and morphology of the aerogel graphene films compared to pure graphene.

5.3. GRAPHENE WITH OXYGEN GROUPS

5.3.1. Graphene with Epoxides and Annulene Groups

An epoxide is a functional group that consists of a three-membered triangular ring containing one oxygen atom and two carbon atoms, as shown in Figure 5.2, with single bonds between each other. The effect of epoxide groups was studied using a 4 x 4 graphene supercell with 32 carbon atoms as the model system, with the amount of oxygen increasing from 1 to 4 atoms per cell, i.e. from 3.03% to 11.11%. In the graphene cells with multiple epoxide groups, different arrangements of epoxide groups were investigated in various configurations. These configurations included pairs and clusters of epoxides, with both close and distant spatial arrangements. Additionally, the relative orientations of the epoxide rings on the same side or on opposite sides of the graphene sheet, designated as "up" and "down," were considered. As shown in Figure 5.3, each structure was named based on the relative positions of the carbon-carbon bonds where the epoxide groups were placed. Additionally, a prime symbol (') was used to denote epoxide groups in up/down arrangements (where one of the epoxide groups was above the graphene plane and the other group was below the plane).

Annulene refers to a cyclic structure with alternating single and double bonds, often leading to aromaticity. In the 4 O zigzag configuration, the C-C sigma bond is broken, creating an annulene-like structure.



Figure 5.2. Showing the Epoxide's Triangular Ring (oxygen-carbon-carbon) Bonds to Graphene's Carbon Lattice. Bond lengths: C-O = 1.461 Å, C-O = 1.461 Å, and C-C beneath O = 1.50 Å after optimization. The C-O-C bond angle is also depicted.

The influence of these different configurations on the stabilities and electronic properties of the structures was then thoroughly analysed (Table 5.1). Based on the calculated energies, the structures with the epoxide groups positioned close to each other (structure "1,3", structure "1,3", structure "1,3',4") were found to be the most stable. Beyond the nearest-neighbour arrangements, there was a weak trend where relatively distant spatial arrangements (such as structures "1,6" and "1,7") were slightly more stable than second and third-neighbour arrangements (such as structures "1,4" and "1,5"). Additionally, Table 5.1 shows that the relative energy variations observed between epoxide structures containing identical epoxide positions but differing orientations were very small, between 0.04-0.24 eV, with up/down arrangements typically more stable than same-side arrangements. This suggests a weak influence of epoxide ring orientation on the overall system energy.

The results in Table 5.1 also show that the energy gain of adding oxygen atoms as epoxide groups (relative to pure graphene and an O_2 molecule) becomes larger as more O atoms are added. Therefore, it is favourable to have more epoxide groups in oxygenated graphene.



Figure 5.3. Graphene Supercells with Various Arrangements of Epoxide Groups and Annulene Groups. Most stable structures are marked with a red box.

Following geometry optimisation, the final structures of graphene with epoxide groups exhibited slight curvatures, deviating from their initial flat, two-dimensional (2D) geometry. This is shown for a select few of the structures in Figure 5.4. This geometric change could potentially influence the behaviour of graphene sheets during aerogel ink fabrication. The introduction of oxygen functionalities can create steric hindrance and electrostatic repulsion between individual sheets, hindering their close packing and ultimately leading to the formation of larger pores in the final aerogel.

Structures	number of Oxygen atoms	Relative Energies (eV)	Energy gain of adding O (eV)	Energy per new C-O bond, kj/mol
Graphene	0			
10	1		-2.19	-105.06
1,3'	2	0.00	-4.88	-117.01
1,3	2	0.04	-4.84	-116.14
1,7'	2	0.20	-4.68	-112.32
1,6'	2	0.26	-4.62	-110.82
1,6	2	0.28	-4.59	-110.22
1,7	2	0.44	-4.43	-106.38
1,5'	2	0.45	-4.42	-106.16
1,4a	2	0.50	-4.37	-104.96
1,4	2	0.52	-4.36	-104.53
1,4a'	2	0.56	-4.32	-103.59
1,5	2	0.60	-4.28	-102.69
1,4'	2	0.64	-4.23	-101.64
1,4,5	3	0.98	-7.06	-112.93
1,3,5	3	0.68	-7.36	-117.69
1,3,4	3	0.36	-7.67	-122.75
1,3',4	3	0.00	-8.04	-128.58
1,2a,9,11a	4	1.47	-11.01	-132.13
1,3,4,7	4	1.16	-11.32	-135.85
NR O Chain	4	1.05	-11.43	-137.13
NR (Z)14,1,9,6	4	0.00	-12.48	-149.73

 Table 5.1 Total energies and relative energies of 4×4 graphene structures with epoxide functional groups; table includes energy gain of adding O and Fermi energies (eV)

The energy gain of adding oxygen (ΔE) is calculated using the following equation:

$$\Delta E = E_{tot}(n) - E_{tot}(n-1) \tag{5.2}$$

Where $E_{tot}(n)$ is the total energy of the structure containing oxygen atoms. $E_{tot}(n-1)$ is the total energy of the structure containing oxygen atoms.

The energy per newly formed C-O bond is calculated as:

$$E_{\rm C-O}bond = \frac{\Delta E \times 96.485}{n}$$
(5.3)

Where 96.485 is the conversion factor from eV to kJ/mol and is the number of newly formed C-O bonds.



Figure 5.4. Curvature Induced by Epoxidation. Following Geometry Optimisation, Graphene Structures with Epoxide Groups Exhibit Slight Curvatures, Deviating from their Initial Flat Geometry.

5.3.1.1. Electronic Structure



Figure 5.5. Graphs Depicting the Density of States of 4×4 Graphene with Epoxide Groups Compared to Pure Graphene. (a) DOS Graphs of Graphene with an Increasing Number of Epoxide Groups, with the Projected DOS of Oxygen Atoms Shown in Red. (b) DOS Graphs of All Structures with Two Epoxide Groups. (c) DOS of Selected Structures with Two Epoxide Groups, where the Contribution of Oxygen Atoms are Shown in Red.

Understanding the density of electronic states and the position of the Fermi energy is crucial for understanding and controlling the electrical and thermal properties of materials, such as graphene. In the case of graphene, the Fermi energy level directly influences its electrical conductivity and can be significantly adjusted through methods like doping.¹⁴ However, the introduction of oxygen atoms can disrupt the pristine electronic structure of graphene, leading to the creation of localised states within the band gap of the material's electronic band structure. This disruption may cause the Fermi energy level to shift away from the Dirac point. This shift in the Fermi energy level due to the presence of oxygen has important implications for the electronic and thermal properties of graphene. It notably

can impact conductivity, and as the Fermi level moves further from the Dirac point, graphene can transition from a semi-metal to a metallic state, potentially affecting its suitability for various applications.

The results in Table 5.1 show that the Fermi energies of epoxide-containing graphene structures have a weak dependence on the amount of oxygen: the structures with more oxygen have slightly more negative Fermi energies, consistent with their higher electronegativity.

This study examined the DOS of graphene with epoxide groups and compared them to those of pure graphene. The DOS data were analysed within the range of -5 to +5 eV around the graphene Dirac point.⁵ The Fermi level for each material was shifted to 0 eV. The DOS analysis provides valuable insights into the electronic properties of graphene with epoxide groups, which can be useful in the development of new materials and technologies.

Figure 5.5 (a) illustrates DOS plots of graphene with different concentrations and arrangements of epoxide groups. The figure shows that the concentration and arrangement of epoxide groups have a direct effect on the DOS and on the opening of band gaps. The structures with few epoxide groups are broadly graphene-like, while structures with more (3 or 4) epoxide groups have prominent new peaks in the valence and conduction band. Band gap opening can be seen in the structure with three epoxide groups and in some of the structures with two epoxide groups.

The partial, or projected, density of states (PDOS) graphs were presented to determine the effect of oxygen. The new large peaks at 1-2 eV below the Fermi level observed in the total DOS as compared to the pure Graphene DOS were attributable to the PDOS of oxygen.

PDOS of all graphene structures with two epoxide groups, compared to that of pure graphene, are depicted in Figure 5.5 (b), and several representative structures are shown in higher magnification in Figure 5.5 (c). Band gap opening is evident in some of the structures. There is a clear relationship between the stabilities of the structures and their band gaps. However, there is a relationship between band gaps and distances between epoxide groups: the structures with nearest-neighbour epoxide groups ("1,3" and "1,3"") have zero band gaps, the structures with nearby epoxide groups (structures based on "1,4" and "1,5" positions) have zero or very small band gaps, while the structures with epoxide groups spaced far from each other (especially "1,6", "1,6", "1,7" and "1,7") have sizeable band gaps of 0.5 - 1.4 eV. Band gaps are discussed in more detail below, together with band structure plots. Projected DOS of the oxygen atoms for several two-epoxide systems are shown in Figure 5.5 (c). PDOS analysis reveals that oxygen modifies the electronic structure of graphene, regardless of the position of the epoxide groups. In particular, oxygen-related peaks appear at 1.8-2.0 eV below the Fermi level in all structures. Moreover, a number of smaller peaks appear in the DOS of all epoxide containing structures.

Analysis of PDOS of individual carbon atoms at different distances from the epoxide shown in Figure 5.6 illustrates that the PDOS of carbon atoms varies depending on their proximity to the epoxide group. The PDOS of atoms C11 and C19, which are directly involved in the epoxide group, are not graphene-like, with no peaks at approximately +/- 2 eV that are seen in graphene DOS in Figure 5.5 (a). Atoms C13 and C18, which are next to two epoxide groups, have peaks that are close to the Fermi level, at +/- 1 eV. In comparison, atoms C10 and C26, which are next to one epoxide group, have PDOS peaks at +/- 2 eV, similar to graphene, although their PDOS still shows additional small peaks compared to pure graphene. Thus, it is clear that C atoms that are closest to the epoxide group are most disturbed by the presence of oxygen.



Figure 5.6. Projected DOS Graphs of Carbon Atoms Around the Epoxide Groups for Structure Named 1,4 (20).

A combination of these graphene-like and non-graphene-like carbons results in the total DOS being different from pure graphene.



Figure 5.7. Projected DOS Graphs of Carbon Atoms Close and Far from the Epoxide Group in a 8×8 Graphene Unit Cell with One Epoxide Group.

To investigate further the extent of the epoxide group's influence on nearby carbon atoms, this study investigated PDOS of carbons at a low concentration of oxygen in graphene, in a 8×8 graphene supercell that contained 128 carbon atoms and an oxygen concentration of just 0.78%. This is visualised in Figure 5.7, which shows the projected DOS of carbon atoms close to and far from the epoxide group in an 8x8 graphene unit cell. The overall density of states revealed a high degree of similarity to pure graphene. However, a closer look at the PDOS of oxygen atoms and the surrounding carbon atoms revealed key differences. The carbon atoms bonded to the oxygen atoms, forming epoxide groups, exhibited a significantly altered PDOS compared to pristine graphene, similar to the equivalent carbon atoms in the 4×4 cell shown in Figure 5.6. In contrast, the PDOS of carbon atoms further away from the oxygen incorporation sites more closely resembled graphene. For example, atom C21 (second nearest neighbour of the epoxide group) displays peaks at -2 and +2 eV, but these peaks are less sharp than in pure graphene. These peaks become sharper in the next most distant atom C20, while further removed atoms such as C11, C1 and C30 show almost graphene-like DOS. These findings suggest that the presence of oxygen in the graphene structure induces localised electronic changes around the epoxide sites, within 3 C-C bonds from the epoxide group, but beyond that distance the overall electronic structure of graphene is largely preserved.

5.3.1.2. Band Structures and Band Gap Opening

The calculated band structures of graphene with epoxides are plotted for six representative structures in Figure 5.8, with the Fermi level denoted by a red dashed line. These plots offer a more precise visualisation of the band gap opening, as the spatial distribution of epoxides varies and their concentration increases. Band structures were similarly plotted for all epoxide arrangements, and band gaps were extracted and summarised in Table 5.2.



Figure 5.8. Band Structures of Graphene with Different Arrangements of Epoxide Groups

number of Oxygen atoms	structure	Direct bandgap Eg (eV)	Type of band Gap
1	10	0.01	zero-gap semiconductor
2	1,4a	0.14	Low-gap Semiconductors
2	1,3	0.21	Low-gap Semiconductors
2	1,3'	0.25	Low-gap Semiconductors
2	1,4a'	0.27	Low-gap Semiconductors
2	1,5'	0.39	Low-gap Semiconductors
2	1,5	0.42	Low-gap Semiconductors
2	1,7'	0.50	Low-gap Semiconductors
2	1,7	0.53	Low-gap Semiconductors
2	1,4	0.55	Low-gap Semiconductors
2	1,4'	0.63	Low-gap Semiconductors
2	1,6	1.15	Low-gap Semiconductors
2	1,6'	1.42	Medium gap semiconductors
3	1,3,5	0.40	Low-gap Semiconductors
3	1,3,4	0.73	Low-gap Semiconductors
3	1,3',4	1.01	Low-gap Semiconductors
3	1,4,5	1.20	Low-gap Semiconductors
4	1,3,4,7	0.18	Low-gap Semiconductors
4	1,2a,9,11a	0.90	Low-gap Semiconductors

 Table 5.2 Calculated band gap values for graphene with epoxide groups.

Figure 5.8 and Table 5.2 illustrate how increasing epoxide functionalisation in graphene influences its electronic structure. The introduction of epoxide groups disrupts electronic conjugation, contributing to an increase in the band gap. The band gap starts opening after at least two epoxide groups (5.89% O) are introduced, transitioning graphene from a semimetal to a semiconductor. The data indicate that epoxide-containing graphene spans different electronic classifications, from zero-gap semiconductors (e.g., 10, with Eg \sim 0.01 eV) to low-gap semiconductors (e.g., structures with band gaps between 0.14 eV and 1.20 eV) and even medium-gap semiconductors (such as 1,6', Eg = 1.42 eV). These results confirm that not only the number of epoxide groups but also their distribution significantly influences the band gap of graphene.

A computational study by Leconte et al. (2010) found that epoxide functionalisation modifies the conductivity and band structure of graphene through orbital rehybridization.¹⁵ Their results show that epoxide groups induce strong intervalley scattering and affect conduction properties. They observed that epoxide coverage from around 0.1% to 4% led to a transition from diffusive to localized transport, with significant disorder effects emerging at higher oxygen content. In their study, epoxide groups were found to induce a metal-insulator transition in graphene, which is consistent with the findings in this research on increasing band gap with oxygen incorporation.

Importantly, the calculations from the 2010 paper indicated that the presence of epoxides leads to symmetry breaking at the K-point, resulting in the opening of a band gap while preserving a zero gap near the K' point. This phenomenon is consistent with our results, which show that the band gaps strongly depend on the positioning of the epoxide groups.¹⁵

Additionally, Leconte et al. also reported that graphene functionalisation with epoxides does not introduce mid-gap states, as both sublattices are affected equally by the defects. This is particularly relevant, as it contrasts with other functionalisations such as hydrogenation or vacancy creation, which can induce localized states.¹⁵ Our study also confirms that the distribution of epoxide groups

influences band gap variations, as seen in the different gaps observed for structures like "1,4" and "1,4", despite their similar oxygen content.

Additionally, previous work form the group has demonstrated similar trends in oxygen functionalisation affecting the conductivity of graphene.¹⁶ These findings support the hypothesis that epoxide-induced modifications significantly impact graphene's band gap and overall electronic properties. This comparison strengthens the argument that the electronic structure of graphene is highly sensitive to oxygen content, symmetry breaking, and disorder effects, emphasizing the need for controlled functionalisation to fine-tune graphene-based electronic devices.

5.3.1.3. Optical Properties of Epoxide-Containing Graphene

The optical properties of graphene with epoxide groups were computed and presented in Figure 5.9 The calculated spectra revealed that as oxygen concentration increased, the maximum absorbance at apx. 300 nm decreased, and additional peaks appeared in the long wavelength region. In particular, in some of the structures (structure "1,7", structure "1,7'" and the structures with four epoxides) the main absorption peak attributed to the $\pi \rightarrow \pi^*$ transition exhibited a blue shift to ~ 240 nm, consistent with a widened spacing between the bands responsible for this transition. Additionally, the presence of further peaks around this region might be indicative of $n \rightarrow \pi^*$ transitions associated with the C-O bonds. Spectra of the structures containing 1 or 2 epoxides (3-6% oxygen) can be described as graphene-like spectra with broadened and lower-intensity peaks, while the spectra of the structures with higher oxygen content are increasingly not graphene-like.



Figure 5.9. Calculated Absorbance of (a) Graphene (G) with an Increasing Number of Epoxide groups, (b) all Graphene Structures with Two Epoxide Groups, (c) Graphene with Three Epoxide Groups, and (d) Graphene with Four Oxygen Groups, All Data Cropped from 200 nm to 800 nm to Match the Experimental Range.

In conclusion, the results presented in this section show that the incorporation of oxygen groups, such as epoxides, into graphene results in changes to the electronic properties, such as the opening of a band gap, thereby modifying graphene's optical properties and changing its conductivity. These modifications can render the materials more reactive to external stimuli, making them suitable candidates for sensor-related applications. Electrical sensors function by detecting changes in electrical properties as a result of interaction with target molecules. The altered electronic structure of graphene carbon atoms next to epoxide groups makes them more reactive, and potentially more sensitive to adsorbates compared to pristine graphene, thereby potentially leading to a stronger signal upon encountering the target molecule and improving the sensor's overall sensitivity. The introduction of oxygen groups in graphene can also act as specific recognition sites for certain target molecules, due to these molecules' chemical affinity for the electronegative oxygen atoms. This can lead to more targeted interaction compared to pristine graphene, thereby enhancing the sensor's sensitivity and selectivity.^{17,18}

5.3.2 Graphene Nanoribbons (GNRs)

Graphene nanoribbons (GNRs) are one-dimensional forms of graphene with finite width. These graphene-derived materials have interesting properties which are different from the properties of pure graphene sheets.¹⁹ The configuration of atoms located along the edges of graphene nanoribbons results in distinctive electronic states that are concentrated around the Fermi level. These edge states play a crucial role in governing the electrical conductivity of GNRs.^{20,21}

Reconfiguring graphene into narrow nanoribbons could result in the introduction of a band gap, thereby facilitating the modulation of on/off behaviours, such as those observed in a transistor. The band gap size is dependent on various factors, such as the nanoribbon's edge state. "Armchair" edges have the potential to be metallic or semiconducting, while "zigzag" edges are metallic. Additionally, the width of the nanoribbon plays a role, as narrower GNRs typically have larger band gaps. Graphene nanoribbons can also be modelled by hydrogen terminations or functionalising of graphene with specific chemical groups.²²



(4 O) Nanoribbon with a chain of epoxides

(4 O) Nanoribbon Zigzag



In this work, a novel approach is presented, involving the functionalisation of graphene with epoxide groups along either zigzag direction and also in a chain of epoxides to produce GNRs as depicted in

Figure 5.10. This approach facilitates the incorporation of oxygen groups, while also allowing for the fabrication of nanoribbons with novel chemistries. The GNR structure with a chain of epoxides formed in this process can be categorised as a nanoribbon as a result of the sp³ hybridisation of carbon atoms bonded to oxygen groups. This hybridisation disrupts the continuous sp²-hybridised carbon lattice that is characteristic of pristine graphene sheets.

Additionally, the zigzag configuration is observed to form annulene structures, where the C-C sigma bond is broken. The zigzag configuration does not form epoxide groups because the oxygen atoms induce structural rearrangement, leading to C-C bond breaking and the formation of conjugated annulene rings instead of maintaining the typical three-membered epoxide structures.

The optimised structures of the GNR with a chain of epoxides and zigzag GNRs with epoxide functionalisation reveal intriguing geometric features. The GNR with a chain of epoxides exhibits slight buckling or some curvature, observations of oxygenated two-dimensional graphene containing epoxide groups. This suggests a consistent interplay between oxygen functionalisation and the formation of non-planar structures. In contrast, the zigzag GNR displays a more pronounced buckling effect due to the incorporation of oxygen atoms, deviating significantly from the pristine planar geometry typically observed in GNRs. This buckling phenomenon, noted upon introducing oxygen atoms at specific concentrations (11%, 17%, and 33%), has been previously reported by Hanna et al. in 2018.²³ Notably, the oxygen concentration in the GNRs in this study, at 11.1%, closely aligns with the range studied by Hanna et al.²³ Both the structures in this study and those described by Hanna et al. contain a continuous row of epoxides. However, unlike the present work, the structures in the study from 2018 do not exhibit broken C-C bonds, possibly due to the difference between a single layer of graphene and the nanoribbon geometry explored here. The crucial factor influencing the observed effects is the presence of a continuous row of epoxides, which disrupts the π -conjugation of the graphene sheet in a highly symmetric manner. This disruption leads to the observed buckling and has significant implications for the electronic properties of the GNRs.

Structure	Fermi energy (eV)	bandgap Eg (eV)	Total energy (eV)
GNR O chain	-5.58	0.70	-6,752.35
Zigzag GNR	-5.29	0.01	-6,753.40

Table 5.3 Bandgap and total energy values for Oxygen containing GNRs.

5.3.2.1. Electronic structure

It can be seen in Table 5.3 and Figure 5.1 that functionalising a GNR with a chain of epoxide groups has introduced an energy gap between the valence and conduction bands. This has led to a significant bandgap of 0.70 eV, which is essential for exhibiting semiconducting behaviour. On the other hand, the zigzag GNR retained a largely metallic character with an almost zero band gap, similar to pure graphene. It is important to acknowledge that numerous studies have explored edge-functionalised graphene nanoribbons, revealing a broad range of electronic properties depending on the edge termination. For example, a study by Nakada et al. (1996) examined the effects of edge shape and size on the electronic properties of hydrogen-terminated GNRs, while a study by Yu et al. (2011) investigated the mechanical and electron-transport properties of pristine GNRs under tensile strain.^{24,25}

Furthermore, Wagner et al. (2013) systematically studied band gap engineering of GNRs via edge functionalisation, considering groups such as hydrogen, fluorine, chlorine, bromine, sulfur atoms, and OH groups. Their findings demonstrated that while armchair GNRs exhibit a tunable band gap depending on the functional group, zigzag and reconstructed Klein-type GNRs show much smaller variations in the band gap, with some functionalised configurations still maintaining small but finite

gaps rather than being strictly metallic. Additionally, their study highlighted that functionalisationinduced geometric distortions, including edge rippling, can significantly influence the electronic properties of GNRs. This was particularly observed for larger functional groups such as chlorine, which induced steric effects leading to out-of-plane distortions. Although Wagner et al. did not explicitly study oxygen functionalisation, they referred to prior works where edge-oxygen-functionalised GNRs were studied. However, in the current work, as mentioned, the GNRs are not edge-functionalised. Instead, a chair or row of oxygen groups is used to modify the GNRs.^{26,27}

Many other studies have demonstrated the crucial role of edge functionalisation in modulating GNR electronic properties, contradicting the notion that the literature has primarily focused on pristine or hydrogen-terminated edges.^{28,29,30}

Unlike previous studies that primarily focused on functionalised terminations, this research introduces a novel structural approach by incorporating annulene groups instead of epoxide functionalisation at zigzag edges.



Figure 5.11. Graphs of the DOS of GNR with a Chain of Epoxides (left) and Zigzag (right) GNRs, with the PDOS of Oxygen Shown in Red.

As illustrated in Figure 5.11, the density of states plots clearly depict the electronic differences between GNR with an epoxide chain and zigzag GNR. The GNR with a chain of epoxides exhibits a clear band gap, while the zigzag GNR retains its semi-metallic character, characterised by the valence and conduction band touching at the Fermi level, similar to graphene. The influence of oxygen groups in both structures is evident by comparing the total DOS with the projected DOS of oxygen (red). Notably, characteristic peaks associated with oxygen states are associated with prominent peaks in the total DOS plots.

The 0.70 eV bandgap of the GNR with an epoxide chain is crucial for causing semiconducting behaviour, which is essential for applications requiring electronic switching, such as in transistors. The results align with earlier theoretical studies of non-functionalised or hydrogen-terminated GNRs,^{24,25} which predicted that even without epoxide functionalisation, chiral or armchair GNRs are expected to exhibit semiconducting properties. The introduction of epoxide groups offers a new synthetic approach to produce GNRs and control their carrier transport and other electronic properties.

In contrast, the zigzag GNR remains largely metallic, showing no significant bandgap, as corroborated by the DOS plots. The distinction between the electronic properties of these GNRs illustrates the significant role of the positioning of oxygen functional groups and the resulting structural deformations, such as buckling, in tailoring the electronic characteristics of GNRs. The data depicted in Figure 5.11 (DOS graphs) and Figure 5.12 (band gaps) illustrate the impact of oxygen incorporation on the atomic arrangement and geometry of GNRs. These structural changes can profoundly influence conductivity, carrier mobility, and other transport characteristics, suggesting that precise functionalisation strategies could be employed to customise the electronic properties of GNRs for specific technological applications. The total energies in Table 5.3 show that the arrangement of epoxides that forms the zigzag GNR is the most stable one, therefore zigzag GNRs are most likely to form by introduction of epoxides.



Figure 5.12. Calculated Band Structures of GNR with a chain of Epoxides (left) and Zigzag (right) GNR with annulene groups.

5.3.2.2. Optical Absorption

Optical absorption spectra of oxygenated graphene nanoribbons were calculated and presented in Figure 5.13, revealing distinct spectral signatures for the zigzag and epoxide chain configurations. The zigzag configuration exhibits prominent peaks at 237 nm and 280 nm, while the GNR with an epoxide chain configuration displays a broader peak centred around 230 nm and another broad peak at approximately 350 nm. Notably, these spectra diverge significantly from that of pure graphene, as they lack a pronounced absorption peak at 300 nm.

The first peak observed in the GNR with the epoxide chain at around 230 nm is tentatively attributed to a shifted π - π * transition involving the aromatic carbon-carbon bonds within the sp²-hybridized carbon domains of the GNRs.

A more detailed analysis, potentially involving DOS and band structure calculations, could provide further insights into the nature of this transition. When oxygen functionalities like epoxide groups are present, they disrupt the conjugation of the π -electron system, which alters the electronic structure of the GNRs and modifies the energy levels involved in the π - π * transitions. The observed red shift of the peak from 295 nm (pure graphene) to around 230 nm indicates that the π - π * transitions is at a higher energy due to the changes in the electronic structure caused by the epoxide groups, in particular the confinement of the 2D π -system into a narrower 1D ribbon. The transitions at around 230 nm are likely to be from flat bands at approx. -8.0 eV to approx. -3.0 eV seen in the band structure of the GNR with an epoxide chain. These bands correspond to DOS peaks at around -2.5 eV in the valence band and +2.3 eV in the conduction band (energies with respect to the Fermi level). It can be seen in the DOS plot that the peaks at around -2.5 eV in the valence band have significant contributions

of O atoms, clearly showing that these transitions are affected by the presence of oxygen in the structure.



Figure 5.13. Calculated Optical Absorption Spectra of GNRs Functionalised with Epoxide and Annulene Groups, Compared to Pure Graphene.

The peaks observed at 280 nm for Zigzag GNR and 350 nm for GNR with an epoxide chain are similarly likely to result from electronic transitions involving both graphene C atoms and O atoms of the epoxide groups. However, it is difficult to pinpoint the exact transitions, as the broadness of the peaks indicates multiple overlapping electronic transitions between several occupied and unoccupied states involving both the epoxide groups and the π -conjugated system of the GNR.

The distinct absorption peak positions for zigzag and GNR with an epoxide chain clearly demonstrate that the structural configurations of GNRs significantly affect their electronic and optical properties. The specific arrangements of epoxide groups in these two types of GNRs create different electronic environments around the C-O bonds and different confinement of the π -systems. This difference influences the energy levels involved in electronic transitions, leading to notable changes in the absorption spectra.

The strong variation in the spectra between zigzag and non-zigzag GNRs suggests that it should be possible to experimentally differentiate these two types of GNRs based on their optical characteristics. Moreover, if these distinct structures can be synthesised, they could potentially be used to harvest sunlight across different spectral ranges due to the complementary nature of their absorption peaks. This property could be particularly useful in developing advanced devices such as LEDs or photosensitisers in solar cells, where the ability to absorb light across a broad spectrum can enhance efficiency and performance.

5.3.3. Graphene with Hydroxyl Groups

The investigation of hydroxyl groups in graphene oxide (GO) and reduced graphene oxide (rGO) is essential due to the presence of these oxygen-containing functional groups, along with epoxides, in these materials. These groups can significantly impact the electronic, optical, and chemical properties of the graphene derivatives. Prior research has demonstrated that the incorporation of hydroxyl groups can alter the electronic properties of graphene, offering the possibility to tailor these properties for specific applications.³¹

When a hydroxyl (OH) group is added to a carbon atom in a graphene lattice, the carbon atom's electronic configuration changes from sp^2 to sp^3 hybridisation. This change occurs due to the creation

of a σ -bond between the sp³ hybridised carbon and the oxygen atom in the OH group. This process alters the electronic properties of the functionalised carbon atom and the surrounding graphene structure. Therefore, hydroxyl groups have the potential to disrupt the π -conjugation of the graphene lattice, resulting in localised changes in electronic structure that may lead to variations in band gap and electrical conductivity.



Figure 5.14. 4×4 Graphene Supercell with Various Arrangements of OH Groups.

The X-ray photoelectron spectroscopy results presented in the previous chapter indicate the presence of oxygen in C-O bonds within the studied samples, confirming the existence of hydroxyl and other oxygen-containing groups. Therefore, understanding the influence of hydroxyl functionalisation is crucial for advancing graphene-based materials with customised properties tailored for applications in sensors.

In this section, the impact of OH groups on the electronic and optical properties of graphene was investigated, and the stabilities and electronic properties of various graphene structures with different numbers and arrangements of OH groups were calculated. Pairs and clusters of four OH groups were considered, to keep the system spin-paired. Similar to the investigation of epoxide groups in the previous section, hydroxyl groups were incorporated in multiple configurations, with both close and distant spatial arrangements (Figure 5.14). Additionally, different orientations of the OH groups relative to the graphene plane, labelled as "up" and "down (')," were also considered.

Table 5.4 displays the total energies and relative energies of different graphene structures with OH groups. The presence of these groups has a significant impact on the system's energies. The spread of relative energies for graphene with hydroxyl groups is much larger than for graphene with epoxide groups, indicating that, unlike epoxides, only the most favourable closely spaced arrangements of hydroxyl groups (structures "Ortho(1, '2)" and "Ortho(1,2)") are likely to form, with results suggesting that OH will prefer to cluster rather than spread homogeneously. This implies that OH functionalisation in graphene will tend to be localized rather than evenly distributed. Moreover, the data suggest that the orientations of OH groups affect the stability and electronic properties of the materials. Structures with opposite orientations lead to lower total energies because out-of-plane distortions compensate each other, reducing overall strain in the system. This suggests that the specific orientation of OH may influence the incorporation of new OH groups.

structures	number of OH groups	Total energies (eV)	Relative energies (eV)	Band Gap Eg (eV)	Band Gap type
Ortho(1',2)	2	-5927.55	0.00	0.32	direct
Ortho(1,2)	2	-5926.95	0.61	0.00	0
Para(1',4)	2	-5926.66	0.90	0.67	direct
1,6	2	-5926.55	1.00	0.00	0
Meta(1',3)	2	-5925.78	1.77	0.01	direct
Para(1,4)	2	-5925.45	2.10	0.66	direct
Meta(1,3)	2	-5924.40	3.16	0.04	indirect
1',5	2	-5924.11	3.44	0.10	direct
1',2',3,10	4	-6828.38	0.00	0.63	direct
1,2,3,10	4	-6826.97	1.41	0.46	direct
1,2',3',10	4	-6824.83	3.55	0.10	direct
1,2',6',7	4	-6824.55	3.83	1.12	direct
1,2,6,7	4	-6823.37	5.01	0.05	indirect

 Table 5.4 Total energies and relative energies of 4×4 graphene structures with OH functional groups, Fermi energies and band gaps (eV)

The stability differences among these configurations can be attributed to a combination of electronic effects and steric interactions. Ortho configurations, where hydroxyl groups are adjacent, tend to be more stable due to possible hydrogen bonding between the hydroxyl groups, which can stabilise the structure by reducing local strain. The closely spaced structure Ortho(1,2), with both OH groups on the same side, is fairly stable, likely due to hydrogen bonding between the hydroxyl groups. This interaction can potentially stabilise the structure.

Meta configurations, where hydroxyl groups are separated by one carbon atom, exhibit reduced stability due to the lack of strong stabilising interactions such as hydrogen bonding, leading to increased local strain. The Meta(1',3) configuration shows lower stability than the ortho configurations, with a very small direct band gap, suggesting it is less electronically favourable.

Para configurations, where hydroxyl groups are positioned opposite each other, can sometimes be more stable due to reduced lattice strain, as the spatial separation minimizes steric hindrance. The Para(1',4) configuration is moderately stable, exhibiting a direct band gap that suggests promising electronic properties. These stability trends reflect the energetic favourability of specific hydroxyl arrangements and their influence on graphene's electronic properties. Notably, research has demonstrated that hydroxyl groups tend to gather in para-positions on one side of the graphene sheet, with the most stable structures for both two and three hydroxyl groups exhibiting para-arrangement.³² This further supports the idea that steric and electronic effects play a crucial role in determining the preferred configurations of hydroxyl functionalization on graphene.

Among the structures containing four OH groups, those with nearest-neighbour positions of OH groups (structures based on the "1,2,3,10" arrangement of OH) are the most stable. In particular, the structure "1',2',3,10" with nearest neighbour OH positions and up/down arrangements that facilitate hydrogen bonding is the most stable. Widely spaced pairs of OH groups (structures based on "1,2,6,7" positions) are less stable. This can be attributed to the distortion of the graphene lattice.

5.3.3.1. Electronic Structures and Band Structures

Figure 5.15 presents a comparative analysis of the DOS for pristine graphene and two graphene structures containing 2 hydroxyl and two structures containing 4 hydroxyl groups in different configurations. The functionalisation of graphene with hydroxyl groups results in a distinct bandgap opening, representing a significant phenomenon in the field. In contrast to pristine graphene, which exhibits metallic characteristics with a zero bandgap, the hydroxylated structures demonstrate observable gaps between the valence and conduction bands. The magnitude of these bandgaps is correlated with the number of hydroxyl groups present; structures containing four hydroxyl groups typically show larger bandgaps than those with two hydroxyl groups.



Figure 5.15. DOS of Pure Graphene (black like), Graphene with 2 OH Groups (in blue) and 4 OH Groups (in green), with the PDOS of Oxygen Shown in Red.

Moreover, the introduction of hydroxyl functionalisation significantly modifies the overall shape of the density of states (DOS). The sharp peaks that are characteristic of pristine graphene broaden, and new states arise within the bandgap due to the presence of hydroxyl groups. These localized states, introduced by the hydroxyl functionalization, can have a considerable effect on the electronic properties of the material. Although all hydroxylated structures illustrated in Figure 5.15 exhibit bandgap openings, the specific arrangement of the hydroxyl groups influences the detailed shape of the DOS. This observation implies that the configuration of hydroxyl groups may affect the electronic properties in ways that extend beyond the simple introduction of a bandgap.

The band structure graphs for the structures discussed above are shown in Figure 5.16, and band gap data are summarised in Table 5.4. Band gap calculations for graphene structures with pairs of OH groups reveal significant variations. Some structures, such as "Ortho(1,2)", "1,6", "Meta(1',3)" and "Meta(1,3)", exhibit zero or near-zero band gaps, suggesting semi-metallic behaviour with free electron movement. Other structures possess small band gaps up to 0.69 eV, characteristic of narrow-gap semiconductors, requiring some energy, such as thermal energy, for conduction. These observations suggest that the arrangement of OH groups is critical in determining the size of the band gap. When the OH groups are positioned very close, such as structures "Ortho(1,2)", or far apart on the graphene sheet, such as structures "1,6", the band gap is negligible. Notably, among these structures with small gaps, the arrangements with OH groups on different sides of the graphene sheet have slightly larger band gaps than same-side arrangements. In contrast, structures "Para(1,4)" and its counterpart "Para(1',4)", where the OH groups are separated by 4 carbon-carbon bonds, show significant band gaps of 0.66-0.69 eV.



Figure 5.16. Calculated Band Structures of Four Selected Graphene Structures with Two or Four OH Groups

The trend in band gaps is less clear in the structures containing 4 OH groups; however, same-side or different-side arrangements seem to have an effect: the structures with all OH on the same side of the graphene sheet (such as "1,2,6,7") tend to have smaller band gaps than the alternatives with OH groups on different sides. Overall, band gaps are larger in structures containing 4 OH than those with two OH.

Based on the results in Table 5.4, it can be concluded that both the number and arrangement of OH groups significantly influence the opening of a band gap in single-layer graphene. Although the presence of 4 OH groups can cause the formation of a band gap, the specific arrangement of these groups has a more substantial impact, as some configurations result in very narrow gaps (0.10-0.18 eV). In cases with only 2 OH groups, their positioning becomes even more critical in determining band gap opening and the size of the band gap.

5.3.3.2. Optical Absorption

Figure 5.17 illustrates the calculated optical absorption spectra for graphene structures with varying numbers and arrangements of OH groups. The presence of hydroxyl groups brings about significant changes in the optical absorption properties of graphene. Specifically, an increase in the number of OH groups generally leads to a reduction in the intensity of the primary absorption peak around 300 nm, accompanied by the emergence of new absorption bands at longer wavelengths, signifying substantial alterations in the electronic structure.





Moreover, graphene structures containing two OH groups exhibit broader absorption peaks compared to pristine graphene, indicating a broader range of electronic transitions, likely due to the disruption of the conjugated π -electron system caused by the introduction of hydroxyl groups. The specific arrangement of hydroxyl groups within the graphene lattice also has an impact on the spectral features, such as the positions and intensities of the shoulder bands.

While structures with two OH groups exhibit relatively consistent profiles, those with four OH groups demonstrate more diverse spectral behaviours. Some configurations result in a blue shift of the primary absorption peak (e.g., green and yellow curves which correspond to the less stable structures), while others cause a red shift (e.g., red and orange curves which correspond to the more stable structures), highlighting the sensitivity of electronic properties to the spatial distribution of OH groups.

Further analysis is needed to fully understand the relationship between bandgap variations and absorption shifts. While bandgap opening may contribute to redshifts in some cases, the prominent absorption peak at \sim 4 eV is not directly related to these changes. However, it is clear that the
arrangement of hydroxyl groups strongly influences electronic transitions, as seen in the spectral features of the structures with four OH groups.

In addition to shifts in peak positions, the intensity of absorption peaks varies with different hydroxyl group arrangements, especially for structures containing 4 OH groups. This variation suggests that the oscillator strengths of the electronic transitions are affected by the presence and configuration of OH groups. The emergence of new absorption bands at longer wavelengths indicates the formation of new electronic states with lower energy gaps, likely associated with the hydroxyl groups. These new states could involve transitions that include the oxygen atoms or altered carbon-carbon bonds.

5.3.4. Oxygen Substitution

The remarkable electrical conductivity of pure graphene is primarily due to its extensive π -conjugated electronic structure. However, when oxygen atoms are introduced as substitutions for carbon atoms in the lattice, the material's electronic properties undergo significant changes. Earlier studies have examined the presence of vacancy-related oxygen (VO) in graphene and similar carbon materials. For example, Lee et al. (1999) were the first to report the incorporation of oxygen at vacancy defects in carbon systems, revealing fundamental structural modifications.³³ Subsequent research by Allouche and Ferro (2006) further investigated oxygen substitution and its effects on electronic properties.³⁴

Recent studies, such as Carlsson et al. (2009), have enhanced our understanding of oxygen-related defects in graphene, emphasizing how substitutional oxygen can alter the electronic structure of graphene.³⁵ Building on these earlier theoretical and experimental studies, Hofer et al. (2019) provided direct evidence of substitutional oxygen in graphene, showing that these oxygen atoms adopt a distinctive triple-coordinated configuration. This structural modification introduces localised defects, which can alter the electronic band structure by creating additional energy states.³⁶ These states may act as scattering centres, reducing the mobility of charge carriers and thus degrading graphene's overall conductivity.

In this work, the presence of substitutional oxygen atoms was analysed to investigate further the impact of oxygen incorporation into the graphene lattice, building on both earlier theoretical and experimental findings. The analysis revealed that oxygen can replace carbon atoms in various configurations, including triple-coordinated oxygen atoms and two-coordinated oxygen atoms positioned both above and below the graphene plane.

The potential role of oxygen substitutional defects as donors or acceptors needs to be carefully examined to fully understand the modifications to the electronic structure caused by these defects. The changes in conductivity can vary, depending on the delicate balance between increased carrier density and the scattering effects induced by these substitutional defects. Consequently, the precise role of substitutional oxygen in graphene remains an area of active research, with significant implications for the design and optimisation of graphene-based electronic devices.³⁷





Figure 5.18 presents the optimised geometries of graphene structures containing one, two, and three substitutional oxygen atoms. In particular, the single substitutional oxygen is three-coordinated, while the pair of oxygen involves two doubly-coordinated O atoms, as suggested previously.³⁶

The structure with three substitutional oxygen atoms is a combination of a single three-coordinated oxygen and a pair of doubly-coordinated oxygens. Unlike the previously discussed epoxide and hydroxyl functionalised systems, these structures exhibit a notable degree of planarity, closely resembling the pristine graphene lattice. The substitution of carbon atoms with oxygen atoms induces minimal structural distortion, preserving the overall hexagonal arrangement of carbon atoms. The exception is the structure with two oxygen atoms, which features one oxygen atom positioned slightly above and the other slightly below the graphene plane. This deviation from perfect planarity is less pronounced compared to the epoxide functionalised systems.

The positioning and coordination of oxygen atoms play a crucial role in altering the electronic properties of the material. As evidenced by the data in Table 5.5, there is a significant decrease in Fermi energies as the number of oxygen atoms increases. This trend suggests that the incorporation of oxygen atoms facilitates electron removal from the oxygen-doped graphene.

Structures	Total Energy (eV)	number of Oxygen atoms	Energy gain of adding O (eV)	Band Gap Eg (eV)	Band Gap type
Graphene	-5,027.54	0		0	0
G with 1 O sub	-5,299.67	1	-272.13	0.19	indirect
G with 2 O sub	-5,576.40	2	-548.86	0	0
G with 3 O sub	-5,848.30	3	-820.76	0.19	direct

Table 5.5 Total energies, Fermi energies and band gaps of graphene with substituted oxygen

5.3.4.1. Electronic Structure

The electronic properties of graphene with substitutional oxygen configurations exhibit substantial differences compared to graphene with oxygen-containing functional groups bound to the basal plane (Figure 5.19). DOS plots show that the presence of oxygen introduces additional peaks around the Fermi level for all structures containing substitutional O. Oxygen PDOS data shows that oxygen atoms contribute to these peaks at the Fermi level, as well as creating new sharp oxygen-dominated peaks in the valence band (the structures with 20 and 30) and in the conduction band (the structure with 1 Oxygen).



Figure 5.19. Density of States Graphs Comparing Pristine Graphene (Black) and Graphene with an Increasing Number of Substituted Oxygens.

A recent DFT study on the electronic properties of graphene with substitutional oxygen atoms revealed that such substitution introduces sharp resonant states near the Dirac point, leading to observed transport asymmetry.³⁷ These resonant states are also evident in the current study, as depicted in Figure 5.19.

As shown in Table 5.5, when oxygen atoms are substituted into the graphene structure, the band gap can increase compared to pure graphene. This is because the oxygen atoms introduce new electronic states that modify the band structure of the material, as shown in Figure 5.19 and Figure 5.20.

The results show that graphene with a pair of substitutional oxygens has zero band gap, like pure graphene, while the structures with one and three substituted oxygens both possess a small band gap of 0.19 eV. Graphene with one substituted oxygen atom has an indirect band gap, while graphene with three oxygen substitutions has a direct band gap. This distinction in the type of band gap is related to the positions of the valence band maximum (VBM) and conduction band minimum (CBM). In materials with a direct band gap, the position of the VBM matches the position of the CBM in the momentum space. This facilitates the excitation of electrons from the valence band to the conduction band, leading to higher conductivity and stronger optical absorption. On the other hand, in materials with an indirect band gap, the position of the top of the valence band does not align with that of the bottom of the conduction band. Consequently, it is more challenging to excite electrons, as excitation requires a change of electron momentum.

Figure 5.20 displays the band structure for the graphene structure with two substitutional oxygen atoms. It can be seen that this system retains a zero bandgap, similar to pristine graphene. The

presence of oxygen introduces additional electronic states, indicated by the new band positioned at the top of the occupied states. This band is associated with a prominent peak in the density of states, approximately 1 eV below the Fermi level, showing a significant contribution from oxygen orbitals.

The retention of the metallic properties in this particular configuration implies that the introduction of oxygen atoms does not inherently create a bandgap in graphene. However, the existence of oxygenderived electronic states within the band structure suggests the potential for altering the electronic properties of graphene through controlled oxygen doping.



Figure 5.20. Top Row: Calculated Band Structures for Graphene with 1 Substitutional Oxygen Atom (Left), 2 Substitutional Oxygen Atoms (Centre) and 3 Substitutional Oxygen Atoms (Right). Bottom Row: Optimised Atomic Structures Corresponding to the Graphs in the Top Row.

5.3.4.2. Optical properties

In Figure 5.21 the calculated absorbance spectra for graphene structures with different levels of oxygen substitution are depicted and compared to pristine graphene. Notably, the maximum absorption decreases as the number of oxygen substitutions increases. Furthermore, similar to the findings on epoxide and hydroxyl-functionalised graphene structures mentioned previously, the introduction of substitutional oxygen leads to a blue shift of the main absorption peak.



Figure 5.21.Calculated Optical Absorbance of Graphene with Substituted Oxygen Compared to Pure Graphene

5.3.5. Discussion

As discussed in Section 5.3, the introduction of oxygen groups disrupts the perfect lattice arrangement of carbon atoms in graphene. This disruption impedes the free movement of electrons across the graphene sheet, potentially diminishing its intrinsic high conductivity. Furthermore, the incorporation of oxygen functional groups can open a band gap in graphene, effectively transforming it from a semimetal to a semiconductor. Generally, the band gap increases with a greater number of oxygen groups; however, the specific orientation and proximity of these groups also plays a significant role in determining the band gap size.

A similar trend was observed in a study by Hanna et al. in 2018, where the band gap of a single graphene sheet increased dramatically, from nearly zero to 2.48 eV, as the oxygen concentration rose.²³ In their work, the focus was on a specific configuration of oxygen impurities within the graphene lattice, differing from the structures examined in this study. The previous study's significant band gap increase can be attributed to the unique arrangement and higher concentration of oxygen groups, which were distinct from those analysed in the work mentioned in section 5.3. This comparison highlights that while both studies investigate the effect of oxygen doping, specific structural differences, such as the type, position, and density of oxygen groups, lead to varying electronic outcomes. The work in this chapter extends on previous studies by providing a comprehensive and systematic investigation of different arrangements and concentrations of oxygen groups. By focusing on systematic exploration, this research aims to thoroughly examine the impacts of these variables on the electronic properties of graphene. The ability to manipulate the band gap opens possibilities for utilising these materials in electronic devices such as sensors, where precise control of conductivity is crucial.

The findings in this research are also comparable with a recent study that utilised DFT calculations to model the effects of oxygen functionalisation on graphene and predicted a widening of the bandgap with increasing oxygen density on the graphene sheet, a result that is consistent with the observations in this section and with their experimental observations.³⁸ While both studies confirm the potential of oxygen functionalisation in tuning the electronic properties of graphene, this thesis builds on these findings by systematically exploring multiple structural configurations and oxygen group orientations that were not previously addressed. The distinct approaches and structural variations considered in this study offer a more comprehensive understanding of how different oxygen functionalisation strategies affect graphene's electronic properties. The research confirms that oxygen treatment can effectively introduce a bandgap in graphene, making it a more suitable material for applications requiring semiconducting properties.

In addition to the changes in electronic and optical properties, our results show that the incorporation of oxygen atoms into the graphene lattice can induce localised ripples. Unlike the distinct buckling observed in the zigzag GNRs, which manifests as pronounced folds, these ripples present as more subtle, localised distortions around the oxygen functional groups. This phenomenon is frequently observed in the optimised structures containing oxygen groups discussed in this section. The formation of these ripples can be attributed to several factors. In the case of substitutional oxygen, is the strain introduced when oxygen atoms, which have different atomic radii (O: 48 pm, C: 67 pm) compared to carbon, replace carbon atoms, or attach to them, forming functional groups. In the case of oxygen functional groups, the conversion of carbon atoms from sp² to sp³ hybridisation due to bonding with oxygen atoms can create structural disruptions. This change in hybridisation and the resulting mismatch in bond lengths can lead to out-of-plane distortions, manifesting as localised ripples or curvatures in the graphene sheet. It is crucial to distinguish these localised ripples from the more common rippling effect seen in pristine graphene. In the latter, ripples are a known characteristic of real graphene sheets at room temperature, resulting from thermal fluctuations and intrinsic instabilities in the two-dimensional lattice. In contrast, the ripples discussed here are specifically associated with the presence of oxygen functional groups and are localised around these sites.

Graphene sheets are inherently hydrophobic due to their non-polar surface.³⁹ However, when oxygen is introduced to graphene, it forms functional groups such as epoxides (C-O-C) and hydroxyls (C-OH), which are polar and are capable of interacting with water molecules and other polar adsorbates through hydrogen bonding. This modification results in enhanced hydrophilicity, allowing oxygen-functionalised graphene to be more easily suspended in water-based solutions. This property is particularly useful when using oxygen-functionalised graphene as a sensor. The oxygen-containing groups on graphene oxide can serve as anchoring sites for attaching other molecules, providing sensitivity and the possibility of selectivity in sensing. This concept is supported by related work in the group demonstrating the preferential binding of phosphates to hydroxyl groups on graphene.¹⁶

5.4. THE EFFECTS OF CURVATURE ON GRAPHENE

5.4.1. Graphene with Curvature

The investigation of curved graphene structures is driven by observations on experimental systems, particularly graphene aerogels, in which curvature and 3D features were visible in TEM images. As detailed in Chapter 4, TEM analysis indicated that oxygen-containing graphene films displayed increased curvature and particle size, corresponding to the extent of oxygen integration. This curvature may originate from the structural strain caused by the incorporation of oxygen atoms, disrupting the graphene lattice and inducing out-of-plane distortions.

To explore the impact of curvature on graphene's structural and electronic properties, a series of curved graphene structures were modelled. A 6x6 graphene lattice served as the base model, which was systematically shrunk by 5% to 20% in either the armchair or zigzag directions. When creating these curved structures, atoms were displaced in the z-direction according to a sinusoidal wave pattern, with the wave amplitude adjusted to ensure that the length along the curve matched the length of the pristine graphene supercell. The final atomic configurations were fully optimised while maintaining fixed lattice parameters, resulting in vertically curved structures.

The graph depicted in Figure 5.22 shows the correlation between relative energies and the percentage of lattice compression for armchair and zigzag configurations. The total and relative energies are presented in Table 5.6. The visual representations of the respective structures demonstrate the impact of varying levels of compression. These structures display significant strain, particularly at the peaks of the curves. Notably, in the A80 and Z80 models (20% compression), the C-C bond lengths at the peaks are shorter, ranging from 1.416 Å in the curved regions to 1.423 Å in the flatter areas. In the zigzag configuration, the bond lengths parallel to the fold and perpendicular to the fold are both 1.424 Å due to uniform bonding. However, in the armchair configuration, the curvature localizes the π -bonding, leading to more pronounced single/double bond character. As a result, the bond lengths parallel to the fold are 1.416 Å, while those perpendicular to the fold are 1.422 Å. This suggests increased strain at the peaks, which likely enhances reactivity in these regions, making them more susceptible to defect formation or the incorporation of functional groups.





The analysis of curved graphene models consistently demonstrates that zigzag structures exhibit greater stability than armchair counterparts, evidenced by lower total energies across varying levels of curvature, ranging from 5% to 20% lattice compression. This finding aligns with the observation that zigzag curved structures are generally more stable than armchair ones, as evidenced by their lower relative energies at similar levels of curvature. Moreover, the relationship between induced strain and structural energy is shown to be linear, with relative energy increasing linearly with the degree of curvature. Table 5.6 presents the total energies for the two types of curvature, demonstrating the higher stability of zigzag curved structures compared to armchair ones.

Curvature	Zigzag	Total Energy (eV)	Relative Energies (eV)	Armchair	Total Energy (eV)	Relative Energies (eV)
0	G 6by6	-11312.3	0	G 6by6	-11312.3	0
5%	Z95	-11309.5	2.764043	A95	-11308.7	3.564043
10%	Z90	-11306.8	5.464043	A90	-11305.1	7.164043
15%	Z85	-11304.1	8.164043	A85	-11301.4	10.86404
20%	Z80	-11301.4	10.86404	A80	-11297.7	14.56404

Table 5.6 Calculated total and Fermi energies of curved graphene structures

5.4.1.1. Electronic structure

Figure 5.23 and Figure 5.24 show that in both zigzag and armchair configurations, the Dirac point remains unchanged despite the introduction of curvature. This indicates that the fundamental semimetallic properties of graphene persist across all studied structures. Examination of the electronic structure near the Fermi level confirms no significant bandgap opening, signalling that the introduction of curvature alone is insufficient to transform graphene from a semi-metal to a semiconductor.



Figure 5.23. Density of States for Zigzag and Armchair Curved Graphene Structures. DOS Spectra For Zigzag (Left) and Armchair (Right) Curved Graphene Models at Compressed Lattice Parameters Of 80%, 85%, 90%, And 95%, Compared to Pristine Graphene.

Upon a detailed analysis of the DOS, subtle changes induced by the curvature are revealed (Figure 5.23). While the DOS near the Dirac point remains characteristic of semi-metallic graphene, small additional peaks emerge in the conduction band. These newly formed peaks indicate the presence of localised electronic states, attributed to the curvature-induced strain and alterations in the local electronic environment. Notably, the variation in the height and position of these additional peaks implies that the curvature impacts the distribution of electronic states, potentially leading to alterations in allowed electronic transitions and subsequent electronic properties.

The influence of the direction of the curvature on the electronic properties is clearly seen in both the DOS in Figure 5.23 and band structures in Figure 5.24. Zigzag curved structures demonstrate a more significant retention of the semi-metallic characteristics, with minimal additional peaks in the DOS. Conversely, armchair-curved structures exhibit a slightly more pronounced change in the DOS, with more noticeable additional states. These distinctions can be attributed to the varying distribution of strain induced by the two types of curvature.

Furthermore, small changes are seen in Fermi energies presented in Table 5.6, which become slightly more negative with curvature in zigzag configurations, and become slightly less negative in armchair configurations.



Figure 5.24. Band structures of zigzag (left) and armchair (right) curved graphene models at 20% compression.

5.4.1.2. Optical Properties

The optical absorption spectra shown in Figure 5.25 reveal interesting differences between curved graphene models, such as zigzag and armchair, and the spectrum of flat graphene. One significant observation is the red shift of the intense π - π * transition peak, which is centred around 300 nm in flat graphene. This red shift occurs in both zigzag and armchair curved structures, with the armchair configuration showing a more pronounced effect. The redshift indicates a reduction in the energy required for electronic transitions, suggesting changes in the electronic structure due to the introduction of curvature.

In general, the absorbance of the curved graphene models is lower compared to that of flat graphene, especially in the near-UV region. Additionally, the absorption spectra display broadening, characterised by the appearance of shoulder peaks at longer wavelengths. This broadening implies a wider distribution of electronic states contributing to the absorption process, likely due to the perturbation of the electronic structure by the curvature, as seen in the DOS plots in Figure 5.23. The

red shift and broadening observed in the absorption spectra of curved graphene models align with experimental findings from aerogel graphene films with higher oxygen content, as discussed in Chapter 4. These films frequently show similar spectral features, including a red-shifted primary peak and broadened absorption. This correspondence suggests that curvature, possibly brought about by oxygen functionalisation, strongly impacts the optical properties of graphene.



Figure 5.25. Optical Absorption Spectra of Curved Graphene

The changes in the optical absorption spectra can be attributed to several factors. Curvature-induced strain and variations in bond lengths can modify the energy levels of electronic states, resulting in shifts in absorption peaks. Additionally, curvature can create new states that broaden the absorption spectra and generate shoulder peaks. These explanations are supported by the density of states data, which reveal additional peaks in curved graphene structures adjacent to the prominent peaks in the valence band (VB) and conduction band (CB). These peaks are slightly closer to the Fermi energy, requiring smaller excitation energies and resulting in a redshift.

Moreover, the introduction of curvature can alter the symmetry of the electronic states, thereby impacting the optical absorption properties. Specifically, the curvature-induced symmetry breaking may enable electronic transitions that were previously prohibited in flat graphene.

Furthermore, enhanced electron-phonon coupling is possible: the lattice distortions caused by curvature may amplify electron-phonon interactions, thereby contributing to the vibrational broadening of the absorption band.

5.4.2. Curved graphene with oxygen groups

Experimental results in Chapter 4 suggest that the incorporation of oxygen into graphene and the resulting curvature significantly alter its fundamental properties. TEM images demonstrate that higher oxygen levels are associated with increased curvature, supporting the idea that oxygen atoms can induce significant structural changes within the graphene framework. These structural modifications influence not only the physical traits of the material but also its electronic and energetic properties, particularly the stability of oxygen incorporation in curved versus flat regions.

To investigate the interplay of curvature and oxygen, oxygen functionalisation was introduced in curved graphene structures in both zigzag and armchair configurations. A single oxygen atom was introduced through substitution in the zigzag configuration with 20% curvature. An epoxide group was incorporated in the armchair configuration with the same 20% curvature. These functionalised structures were subsequently optimised, with the resulting geometries shown in Figure 5.26 and their relative energies, stated in Table 5.7.

Although a direct numerical comparison to the flat graphene models from Section 5.3 is not possible due to differences in system size (4×4 for flat models vs. 6×6 for curved models), the general trend in oxygen stability can still be assessed. The energy gained from oxygen addition provides insight into whether oxygen prefers to bind in curved or flat regions. For Z80 graphene, the energy gain of substitutional oxygen incorporation is +154.78 eV, whereas for A80 graphene, adding an epoxide group results in an energy change of -5.18 eV. These values suggest that oxygen incorporation strongly depends on both curvature and bonding configuration, with substitutional oxygen being significantly more stable in the zigzag curved graphene, while epoxide formation in the armchair configuration is energetically less favourable.



Z80 and 1 Oxygen Substitution

A80 and 1 Epoxide Group

Figure 5.26. Curved Graphene with Oxygen Groups: (left) Substitutional Oxygen in Z80 Zigzag Curved Graphene, (right) Epoxide Group in A80 Armchair Curved Graphene.

Structure	Total Energy (eV)	Number of Oxygen Atoms	Energy Gain of Adding O (eV)
Z80 Graphene	-11301.40	0.00	
Z80 with 1 Substitutional Oxygen	-11574.96	1.00	154.78
A80 Graphene	-11297.70	0.00	
A80 with 1 Epoxide Group	-11731.22	1.00	-5.18

Table 5.7 Relative Energies of Curved Graphene Structures with Oxygen Groups

5.4.2.1. Electronic Properties

The analysis of the DOS depicted in Figure 5.27 offers insight into the electronic properties resulting from curvature and oxygen functionalisation. In the pristine Z80 configuration (20% zigzag curvature), the DOS displays typical graphene-like characteristics with sharp peaks at \pm 2 eV above and below the Fermi level and zero DOS at the Fermi level, indicating the preservation of its semi-metallic nature. However, upon the introduction of a substitutional oxygen atom, appearance of a new peak below the Fermi level and a noticeable broadening of the DOS features becomes apparent. This broadening implies the presence of new electronic states, possibly arising from the loss of symmetry or from the perturbation of the π -electron system by the oxygen atom. The new peak below the Fermi level suggests a change in the band structure and the formation of a localised state around the oxygen site.

For the A80 configuration (20% armchair curvature), the DOS also retains semi-metallic behaviour, though the effects of oxygen functionalisation are more subtle compared to the zigzag configuration. When an epoxide group is introduced, there is only minor broadening of the DOS near the Fermi level, suggesting minimal alterations to the electronic structure. In contrast, the substitutional oxygen in Z80 causes more substantial changes, including the formation of the peak, as mentioned earlier, below the Fermi level. This indicates that substitutional oxygen atoms introduce localised states that

significantly impact the electronic properties and reactivity of the material, a more pronounced effect than that caused by epoxide functionalisation.



Figure 5.27. The Total and Projected Oxygen (O) Density of States for Curved Zigzag and Armchair Graphene Structures. Z80 And A80, Compared with Z80 with a Substitutional Atom and A80 with an Epoxide Group. Optimised Atomic Structures for Each System Are Also Shown.



Figure 5.28. The Band Structures of the Z80+1 O Sub (left) and A80+1 Epoxide (right) Systems. A Dashed Red Line Indicates the Fermi Level.

In the band structures discussed in section 5.4.1 and shown in Figure 5.24, it was observed that the introduction of curvature alone does not result in a band gap opening in graphene. However, when curvature is combined with oxygen incorporation (Figure 5.28) through the addition of a substitutional oxygen atom, a small band gap of approximately 0.2 eV is formed, similar to flat graphene with 1

substitutional oxygen. While the material can still be classified as semi-metallic with a small gap, further exploration into the impact of increased oxygen content may lead to the formation of a larger band gap, as seen in the example of flat oxygenated graphene (Section 5.3).

5.4.2.2. Optical Properties

Figure 5.29 displays the optical spectra of curved graphene structures with oxygen functional groups and compares them with those of pure graphene and curved graphene. Pure graphene displays a sharp, intense absorption peak at approximately 300 nm, attributed to the π - π * electronic transition within the sp² carbon network. The presence of curvature, as seen in Z80 and A80, causes this peak to broaden and shift slightly towards the red end of the spectrum, indicating perturbations in electronic transitions.



Figure 5.29. Calculated Optical Absorption Spectra of (a) Pristine Graphene, Zigzag Curved Graphene Z80, and Z80 with a Single Substitutional Oxygen Atom (Z80 + 1 O Sub); (b) Pristine Graphene, Armchair Curved Graphene A80, and A80 with a Single Epoxide Group (A80 + 1 epoxide). The spectra were cropped in the wavelength range of 200-800 nm.

Introducing oxygen functional groups, including substitutional oxygen and epoxide groups, contributes to subtle spectral changes in the material. The absorption peaks become slightly broader, demonstrate a more pronounced red shift, and reveal the emergence of a distinct shoulder in the range of 350-400 nm. These modifications suggest the presence of new electronic states associated with the oxygen functional groups, which interact with the graphene π -electron system. Collectively, these spectral alterations highlight the influence of curvature and oxygen integration on graphene's electronic structure. However, the changes induced by oxygen appear to be relatively minor compared to those observed in flat graphene.

Given these findings, it is plausible that higher oxygen content could lead to more significant alterations. However, based on the current data, spectroscopic techniques seem unlikely to effectively differentiate between curved graphene with and without oxygen functionalisation for the levels studied.

5.4.3. Discussion

The study delved into the effects of curvature with oxygen functionalisation on the electronic characteristics of graphene by simulating various curved graphene configurations. This included investigating curved graphene structures with and without oxygen functionalities to replicate the properties of aerogel graphene samples and gain insights into their behaviour.

Examination of the strain present in these curved graphene structures reveals significant variations in the distances between carbon-carbon (C-C) bonds, especially in the more highly curved areas. These

variations are a result of compressive strain and the resulting out-of-plane displacements. It is worth noting that in configurations such as A80 and Z80 (which undergo 20% compression), the C-C bond lengths at the peaks of the curves are shorter than those in the flatter regions. In the curved areas of the Z80 model, as previously stated, the carbon-carbon bond lengths range from 1.416 Å in the curved parts and 1.423 Å in the flatter parts. This bond shortening indicates increased strain, suggesting that these more distorted areas may act as active sites for adsorption or the introduction of defects. Such sites are energetically favourable for interactions with other atoms or molecules, making them crucial for potential catalytic applications or further chemical modifications.

The research uncovered that zigzag curved graphene structures tend to be more stable than their armchair counterparts, as indicated by lower total energies across different levels of curvature. This increased stability is likely due to variations in strain distribution between the two configurations. Despite these structural alterations, both configurations retained the Dirac point, indicating the preservation of graphene's essential semi-metallic properties. However, subtle changes in the density of states near the Fermi level, particularly the appearance of new peaks, indicate the formation of localised electronic states caused by curvature-induced strain.

The optical absorption spectra of curved and oxygen-functionalised graphene samples exhibited subtle changes and a slight red shift compared to pristine graphene. The red shift of the intense π - π * transition peak and peak broadening signify an altered electronic structure due to curvature and strain. The spectra were further red-shifted, and additional shoulder peaks appeared with the introduction of oxygen functionalities.

These findings emphasise the complex impact of curvature and oxygen incorporation on the electronic and optical properties of graphene. Curvature induces strain, leading to alterations in the electronic structure and the introduction of new electronic states. Oxygen functionalisation further enhances these effects, showcasing the potential for control over the material's characteristics. Such control is imperative for applications in sensor technologies, where specific electronic and optical properties are sought after.

Further research should concentrate on investigating other types of functional groups and higher levels of oxygen content, as this may reveal stronger changes, potentially including the formation of a significant bandgap in graphene. This could expand its applicability in electronic and optoelectronic devices. While these structures were being considered and calculations were started, they were not completed within the given time frame.

5.5. GRAPHENE WITH A MONOVACANCY AND OTHER DEFECTS

Defects in graphene can significantly modify its inherent physical and chemical properties, resulting in noticeable changes in its behaviour and potential applications. These imperfections in the otherwise flawless hexagonal lattice structure of graphene can introduce localised variations in electronic, mechanical, and chemical characteristics. Specifically, defects can disrupt the bonding of carbon atoms, leading to the formation of dangling bonds, changes in bond lengths and angles, and the creation of localised strain fields. Such alterations can have a significant impact on electronic properties by introducing states within the band gap, affecting charge carrier mobility, and altering magnetic properties. In their 2010 paper, Banhart, Kotakoski, and Krasheninnikov discussed various types of defects, such as point defects, including monovacancies and Stone-Wales (SW) defects, line defects, and defects at the edges or in multilayer structures.⁴⁰ This section specifically examined the interactions of a monovacancy defect and SW defect with oxygen groups and their effect on the electronic properties of graphene. It is essential to acknowledge that such defects are intrinsic to graphene samples and films. Despite being present at low concentrations, their impact on the material's properties and behaviour can be substantial. Therefore, understanding the traits and behaviour of monovacancies is vital for interpreting experimental findings and predicting the efficacy of graphene-based applications.

5.5.1. Monovacancy Defect and Oxygen Groups

Monovacancy

A monovacancy defect occurs when a single carbon atom is missing from the graphene lattice, resulting in unpaired bonds that increase the material's chemical reactivity. The energy needed to create a single vacancy is high, at around 7.5 eV, indicating that these defects are rare under normal conditions but can be induced through exposure to radiation or chemical processes.⁴⁰

For this section, several structures were considered, as shown in Figure 5.30. Additionally, a graphene structure containing both a monovacancy and an epoxide group was considered. However, the structure underwent relaxation during the optimisation process, resulting in a graphene structure with a single substitutional oxygen atom and no vacancy. As a result, this system was excluded as such structure was already studied in section 5.3.4. The optimised structures, shown in Figure 5.30, include graphene with a single monovacancy, graphene with a monovacancy filled with a substitutional oxygen atom, and graphene with a monovacancy and two hydroxyl (OH) groups. In the case of monovacancy with oxygen substitution, the oxygen atom does not occupy the vacancy site. Instead, it replaces a carbon atom adjacent to the vacancy, capturing the combined effects of both the monovacancy and the oxygen substitution. These structures were studied because monovacancies are common of defects that occur in graphene, and this work aims to understand how the properties of monovacancies are modified by interaction with oxygen groups.



Monovacancy and 1 Oxygen

Substitution

Monovacancy and Two OH

Groups

Figure 5.30. Graphene structures with Different Types of Defects: (a) Monovacancy, (b) Monovacancy and Oxygen Substitution, (c) Monovacancy and Two OH Groups.

Structural analysis reveals significant changes in C-C bond lengths around the defect sites. The monovacancy-only structure displays a shortening of C-C bonds at the vacancy site to around 1.40 Å. In contrast, in the structure with a monovacancy and two hydroxyl groups, C-C bonds adjacent to hydroxyl groups become elongated, measuring approximately 1.50 Å, while those at the vacancy site far from the hydroxyl groups are shortened to 1.41 Å. Similarly, in the structure with a monovacancy and one substitutional oxygen, C-C bonds neighbouring the oxygen atom are elongated to 1.48 Å, and those at the undercoordinated C atom are elongated to 1.44 Å. The shortening of the bonds far from the oxygen groups is consistent with the structure of the isolated vacancy, while the elongation of C-C bonds neighbouring the oxygen atoms suggests a change in the hybridisation of the carbon atoms from sp² to sp³.

Structures	Total Energy (eV)	Number of Carbon atoms	Number of Oxygen atoms	Fermi Energy (eV)	Band Gap Eg (eV)
Graphene	-5027.54	32	0	-5.31	0
Monovacancy	-4863.01	31	0	-5.53	0.20
Monovacancy and 1 O Sub	-5299.92	31	1	-4.95	0.53
Monovacancy and 2OH	-5766.29	31	2	-5.18	0.40

 Table 5.8. Energies, Structural Details and Electronic Properties of Graphene Structures with Vacancies and Oxygen

 Functionalisation

5.5.1.1. Electronic Properties

Figure 5.31 compares the total DOS of pristine graphene with that of graphene modified with monovacancy and oxygen functionalities. The introduction of a single vacancy significantly alters the DOS, introducing new states near the Fermi level that influence the electronic properties of graphene. In this work, we have studied the high-symmetry (3-fold symmetric) vacancy structure; however, it is known that the true ground state is the reconstructed vacancy, as reported by El-Barbary et al.⁴¹

The DOS profile for monovacancy with oxygen substitution exhibits distinct features around the Fermi level, attributed to the interaction between the oxygen atom and nearby carbon atoms. The DOS for hydroxyl groups at a monovacancy shows additional features compared to both pristine graphene and the simple vacancy case, reflecting modifications in the electronic structure due to chemical functionalisation with hydroxyl groups. In summary, the introduction of vacancies, oxygen substitutions, and hydroxyl groups generates new electronic states and significantly alters the electronic structure of graphene.



Figure 5.31. DOS of Pristine Graphene Compared with the DOS Of Graphene with a Monovacancy (1 Vacancy), Graphene with Monovacancy and a Substitutional Oxygen Atom (1 V + 1 O Sub), and Graphene with a Monovacancy and Two Hydroxyl Groups (1 V + 2 OH). The red lines show the PDOS of oxygen.



Figure 5.32. Band Structures of (left) Graphene with a Single Vacancy, (middle) Graphene with a Vacancy and a Substitutional Oxygen Atom, and (right) Graphene with a Vacancy and Two Hydroxyl Groups.

The band structure plots in Figure 5.32 demonstrate that the presence of defects in graphene results in the formation of band gaps. Table 5.8. Energies, Structural Details and Electronic Properties of Graphene Structures with Vacancies and Oxygen Functionalisation provides quantitative information about the band gaps of these structures. When a monovacancy is introduced in graphene, it creates localised states within the band structure, leading to the emergence of a small band gap of 0.20 eV. This signifies a minor change in the electronic properties due to the presence of the vacancy, and the structure can be considered a narrow-gap semiconductor.

Substituting one oxygen atom for a carbon atom at the vacancy site increases the band gap to 0.53 eV. The inclusion of the oxygen atom significantly alters the electronic structure, resulting in a more pronounced band gap compared to the monovacancy alone and compared to a three-coordinated substitutional oxygen structure described in section 5.3.4, resulting in a small band gap semiconductor.

The introduction of two OH groups at the vacancy site produces a band gap of 0.40 eV. It can be seen in Figure 5.32 that, this arrangement introduces new electronic states both above and below the Fermi level, that modify the band structure and the DOS more significantly than the single oxygen substitution.

5.5.1.2. Optical Properties

The optical spectra of the monovacancy-based structures are compared to pure graphene in Figure 5.33. The introduction of a single vacancy into the graphene lattice results in significant changes in the absorption spectrum. The main peak at around 300 nm shows a slight blue shift to shorter wavelengths, indicating a decrease in the energy required for the π - π * transition. This shift is due to modifications in the electronic structure caused by the disruption of the conjugated π -electron system resulting from the vacancy. Moreover, a new absorption band appears around 320-350 nm, suggesting the emergence of localised electronic states associated with the vacancy defect.



Figure 5.33. Absorbance Spectra of Pristine Graphene Compared to Graphene with a Single Vacancy (1 Vacancy), Graphene with a Vacancy and a Substitutional Oxygen Atom (1V + 1 O Sub), and Graphene With a Vacancy and Two Hydroxyl Groups (1V + 2OH).

When a substitutional oxygen atom is introduced at the vacancy, it further alters the absorption spectrum. The main peak becomes less intense and experiences a red shift compared to the single vacancy case, indicating a perturbation of the electronic structure. The shoulder peak around 350-400 nm becomes more pronounced, suggesting an increased contribution of electronic transitions involving the oxygen atom.

The presence of two hydroxyl groups results in a more significant modification of the absorption spectrum. The main peak experiences a noteworthy reduction in intensity and further red-shift. The secondary peak at around 320-400 nm becomes even more prominent, indicating a higher density of electronic states associated with the hydroxyl groups.

The changes observed in the spectra can be attributed to changes in the electronic structure. As seen in Figure 5.32, the introduction of defects and functional groups causes changes in the electronic energy levels of graphene, leading to the observed spectral changes. For example, in the DOS for the structure with one vacancy and two hydroxyl groups, a localised state appears near ~-4.5 eV, which can be attributed to the vacancy and hydroxyl-induced electronic states. Similarly, in the case of the structure with one vacancy and one substitutional oxygen, a new peak emerges near ~-5.5 eV, indicating the presence of localised states due to the substitutional oxygen. These additional states contribute to the emergence of new absorption bands.

5.5.2. Stone-Wales (SW) Defects with Oxygen Groups

The Stone-Wales (SW) defect is a topological irregularity that involves the rotation of a carbon-carbon bond, causing four hexagons to transform into two pentagons and two heptagons without any addition or removal of atoms. This reorganisation maintains the number of carbon atoms in the lattice but results in localised strain, which impacts electronic properties by changing the density of π electrons around the defect. Stone-Wales defects enhance local reactivity and can serve as active sites for chemical reactions.⁴⁰This section investigated the interplay of the SW defect and an epoxide group. Figure 5.34 displays the graphene structures with SW defects examined in this section.



(a) Graphene with SW Defect



(b) Graphene with SW Defect and an Epoxide

Figure 5.34. Graphene Structures with Stone-Wales (SW) Defects: (a) SW Defect, (b) SW Defect with an Epoxide Group.

Structures	Total Energy (eV)	number of Oxygen atoms	Fermi Energy (eV)	Band Gap Eg (eV)
G and 1 epoxide	-5458.08	1	-5.48	0
G SW and 1 epoxide	-5454.31	1	-5.58	0

 Table 5.9. Total energies, Fermi Energies and Band Gaps of Epoxide-Functionalised Graphene and SW-Defected

 Graphene

A comparative analysis of pristine graphene (G) and graphene with SW defect (G SW), each containing a single epoxide functional group, is presented in Table 5.9. Total energy calculations reveal that graphene with one epoxide is significantly more energetically stable than its SW defect counterpart.

This increased stability is due to the inherent instability of the SW defect, which results from its strained structure and unpaired electrons, contributing to its higher energy state.

5.5.2.1. Electronic Properties

The incorporation of a Stone-Wales (SW) defect into the pristine graphene lattice leads to a significant disturbance in the electronic structure, as depicted in Figure 5.35 and Figure 5.36. This structural irregularity, characterised by a 90-degree rotation of two adjacent carbon atoms, disrupts the regular potential experienced by the electrons. As a result, the DOS profile undergoes marked changes. The Stone-Wales defect gives rise to the emergence of localised states within graphene's conduction band. These localised states can serve as electron traps or recombination centres, thereby significantly influencing the material's charge carrier mobility and lifetime. The observed effect is consistent with the findings from Banhart et al. which demonstrated that structural defects, specifically the Stone-Wales defect, in graphene significantly modify its electronic properties. This indicates that the presence of such defects leads to the formation of states that directly impact charge transport mechanisms.⁴⁰



Figure 5.35. Comparison of DOS of Graphene, Stone-Wales (SW) Defect, and SW Defect with Epoxide

The addition of an epoxide functional group to the SW defect causes additional electronic perturbations (Figure 5.35). The oxygen atom in the epoxide group introduces new electronic states to the system, resulting in extra peaks in the DOS spectrum, similar to the case when epoxide was added to pristine graphene. Epoxide-related states interact with existing SW defect states and alter the graphene band structure, leading to intricate modifications in the electronic properties. In Figure 5.36, it can be observed that the band structures of these systems demonstrate subtle changes,

particularly in the case of the SW defect. In particular, the Density of States of the SW defect includes a peak just above the Fermi level, which corresponds to a relatively flat band in the band structure at -5 eV. Remarkably, this feature vanishes upon the addition of an epoxide group, implying that this state is associated with the double bond in the centre of the SW defect. It is likely that the introduction of the epoxide group converts this double bond into a single bond, resulting in the disappearance of the peak.



Figure 5.36. Left panel: Band structure of Graphene with a Stone-Wales (SW) Defect. Right panel: Band Structure of Graphene with a Stone-Wales (SW) Defect and a Single Epoxide Functional Group.

5.5.2.2. Optical Properties

The calculated optical absorbance spectra in Figure 5.37 show that the introduction of the SW defect induces notable changes in the absorption spectrum. A red shift is evident, with the main absorbance peak shifting to approximately 350 nm and reducing in intensity. This spectral shift implies a decrease in the energy gap required for the most intense electronic transition. This is because the SW defect disrupts the extended π -conjugation system, leading to localised electronic states and which cause the new absorbance features. Graphene with SW defect shows increased absorbance compared to pristine graphene in the range of 350-600 nm. A small shoulder peak is also observed at around 230nm.

The introduction of an epoxide functional group to the SW-defected graphene further modifies the absorption profile. A red shift of the peak to approximately 320 nm is observed, with a new intense absorbance peak at approximately 450 nm. This suggests a greater reduction in the energy gap responsible for this principal transition, compared to both graphene and SW-defected graphene. As seen in the DOS plot, the epoxide functional group leads to alterations in the electronic environment and the presence of multiple peaks at around \pm eV instead of single sharp peaks, which in leads to the observed spectral changes.



Figure 5.37. Calculated UV-Vis Absorbance Spectra of Graphene with SW Defects.

5.5.3. Discussion

This section has delved into the impact of defects, specifically monovacancies and SW defects, on the electronic and optical properties of graphene films. Defects are deviations from the ideal hexagonal lattice structure of graphene, which can occur during the synthesis process under real-world conditions. Understanding the effects of these imperfections is crucial, as they can significantly alter the material's behaviour.

Transmission electron microscopy images, detailed in Chapter 4, reveal structures that indicate the presence of these defect types in the graphene samples studies in the experimental part of this project. The study employs theoretical calculations to analyse how these defects affect the electronic and optical properties of graphene.

Our investigation of electronic properties revealed that the introduction of monovacancies in the graphene lattice leads to substantial changes in the electronic structure. Specifically, new localised states appear near the Fermi level, which can influence electrical conductivity and carrier mobility. Monovacancies create a small bandgap, transitioning graphene from semi-metallic to a narrow bandgap semiconductor. These defects cause significant disruptions in the electronic structure due to the rearrangement of carbon atoms. They introduce localised states above or below the Fermi level, which can serve as electron traps or recombination centres, potentially reducing carrier lifetime and altering conductivity.

When oxygen is introduced into the system, the impact on the electronic properties becomes more pronounced. For instance, a monovacancy with a substitutional oxygen atom exhibits a wider bandgap of 0.53 eV compared to 0.20 eV for the monovacancy alone. The presence of oxygen introduces new electronic states that interact with those of the monovacancy, leading to significant modifications in the band structure and density of states. Similarly, the addition of hydroxyl groups to monovacancy results in an increased bandgap of 0.40 eV and introduces additional localised states. These changes are more substantial compared to the effects observed with monovacancies alone, highlighting the role of oxygen in altering graphene's electronic behaviour.

Our investigations of optical properties demonstrated that both monovacancies and SW defects lead to red-shifts in the absorbance spectra, indicating a reduction in the energy required for electronic transitions. This shift suggests a change in the optical bandgap, affecting the material's optical absorption characteristics.

The presence of oxygen functionalities further modifies these optical properties. For example, the addition of a substitutional oxygen atom near a monovacancy results in a more pronounced red shift in the absorption spectrum compared to the monovacancy alone. This indicates a more significant alteration in the optical bandgap due to the interaction between the oxygen atom and the defect site. Similarly, the introduction of two hydroxyl groups leads to a notable reduction in the intensity of the main absorbance peak and a further redshift, reflecting a complex interplay between the hydroxyl groups and the existing defect-induced electronic states.

To conclude, the combined effects of defects and oxygen-functionalised groups provide new insights into tuning the electronic and optical properties of graphene. The incorporation of oxygen into known defects offers a route for more precise control of graphene's properties, offering potential strategies for tailoring the material's behaviour for specific applications.

5.6. CONCLUSION

This thorough examination of the influence of different oxygen functional groups on the electronic and optical properties of graphene uncovers subtle and unique effects, offering valuable insights for precise material enhancements.

In regard to the electronic properties, the introduction of epoxide groups in graphene results in a modest change in the material's electronic structure, causing a slight bandgap opening. The influence of the epoxide group is not as strong as other oxygen functional groups studies in this work, but it is still noteworthy. Hydroxyl groups have a more significant effect on the bandgap compared to epoxides. They effectively increase the bandgap, causing graphene to transition from a semi-metal to a semiconductor to a greater extent. Substitutional oxygen groups have a minimal impact on the bandgap. However, they do introduce new electronic states very close to the Fermi level, which can affect the electronic properties in a way that is distinct from the other oxygen groups.

These differences underscore the potential for strategic use of each type of oxygen group to finely adjust graphene's electronic properties for specific applications. The ability to introduce or modify the bandgap and electronic states can enable tailored adjustments to achieve desired material performance.

Regarding the optical properties, the presence of epoxide and hydroxyl groups brings about significant changes in the optical characteristics of graphene, resulting in noticeable red shifts and broadening in absorption spectra. This suggests substantial modifications to the optical bandgap and electronic transitions. In contrast, the effects on optical properties of substitutional oxygen are relatively minor, with only slight red shifts being observed, consistent with its minimal impact on the bandgap. Similar to substitutional oxygen, curvature-induced changes in the optical properties of curved graphene are relatively small. However, the introduction of curvature does result in subtle alterations in the absorption spectra, albeit less pronounced than those observed with epoxides, hydroxyls and substitutional oxygen.

This research suggests that while epoxide and hydroxyl groups possess the potential to significantly alter the electronic and optical properties of graphene, substitutional oxygen and curvature produce more nuanced changes. This knowledge can be utilised to tailor graphene-based materials for specific applications, such as sensors or optoelectronic devices.

By comparing the findings in this section with the experimental data presented in Chapter 4, particularly regarding the features of the absorption spectra, such as broadening and shifts in peak positions, it can be concluded that the observed experimental samples are more likely to contain structures with curvature and substitutional oxygen rather than hydroxyls and epoxides. The comparison plot of experimental and calculated spectra validates this interpretation (further discussed in Chapter 6), indicating that while hydroxyls and epoxides lead to more pronounced changes, curvature and substitutional oxygen closely align with the experimental observations.

Overall, this study establishes a fundamental understanding of the impact of various oxygen functional groups and structural modifications on graphene, offering the potential for precise control over its properties in a range of technological applications.

5.7. REFERENCES

¹ Lee, K., Murray, É. D., Kong, L., Lundqvist, B. I., & Langreth, D. C. (2010). Higher-accuracy van der Waals density functional. *Physical Review B*, *82*(8). <u>https://doi.org/10.1103/physrevb.82.081101</u>

² Artacho, E., María, J., Barcelona, C., Center, S., Gale, J., García, A., Junquera, J., Martin, R., Papior, N., & Soler, J. (2021). https://siesta-project.org/SIESTA_MATERIAL/Docs/Manuals/siesta-4.1.5.pdf

³ Perdew, J. P., Burke, K., & Ernzerhof, M. (1996). Generalized Gradient Approximation Made Simple. *Physical Review Letters*, 77(18), 3865–3868. https://doi.org/10.1103/physrevlett.77.3865

⁴ J. Oroya, A. Martín, M. Callejo, M.García-Mota, and F. Marchesin in *"Pseudopotential and Numerical Atomic Orbitals Basis Dataset"* https://www.simuneatomistics.com/siesta-pro/siesta-pseudos-and-basis-database/

⁵ A. H. Castro Neto, Guinea, F., N. M. R. Peres, Novoselov, K. S., & Geim, A. K. (2009). The electronic properties of graphene. *Reviews of Modern Physics*, *81*(1), 109–162. <u>https://doi.org/10.1103/revmodphys.81.109</u>

⁶ Wallace, P. R. (1947). The Band Theory of Graphite. *Physical Review*, 71(9), 622–634. https://doi.org/10.1103/physrev.71.622

⁷ Linus Pauling. (1963). The nature of the chemical bond and the structure of molecules and crystals : an introd. to modern structural chemistry. Cornell Univ. Pr.

⁸ Slonczewski, J. C., & Weiss, P. R. (1958). Band Structure of Graphite. *Physical Review*, *109*(2), 272–279. https://doi.org/10.1103/physrev.109.272

⁹ McClure, J. W. (1957). Band Structure of Graphite and de Haas-van Alphen Effect. *Physical Review*, *108*(3), 612–618. <u>https://doi.org/10.1103/physrev.108.612</u>

¹⁰ Jing-Han, Y., Wei-Wei, J., Er-Qiang, L., Tian-Song, P., Yuan-Yuan, Z., & Hui, W. (2010). Fifth-Nearest-Neighbor Tight-Binding Description of Electronic Structure of Graphene. *Communications in Theoretical Physics*, *53*(6), 1172–1176. https://doi.org/10.1088/0253-6102/53/6/36

¹¹ Suzuki, A., Tanabe, M., & Fujita, S. (2017). Electronic Band Structure of Graphene Based on the Rectangular 4-Atom Unit Cell. *Journal of Modern Physics*, *08*(04), 607–621. <u>https://doi.org/10.4236/jmp.2017.84041</u>

¹² Chaves, A., Azadani, J. G., Alsalman, H., da Costa, D. R., Frisenda, R., Chaves, A. J., Song, S. H., Kim, Y. D., He, D., Zhou, J., Castellanos-Gomez, A., Peeters, F. M., Liu, Z., Hinkle, C. L., Oh, S.-H., Ye, P. D., Koester, S. J., Lee, Y. H., Avouris, Ph., & Wang, X. (2020). Bandgap engineering of two-dimensional semiconductor materials. *Npj 2D Materials and Applications*, *4*(1). https://doi.org/10.1038/s41699-020-00162-4

¹³ Kim, S., Hwang, S. W., Kim, M.-K., Shin, D. Y., Shin, D. H., Kim, C. O., Yang, S. B., Park, J. H., Hwang, E., Choi, S.-H., Ko, G., Sim, S., Sone, C., Choi, H. J., Bae, S., & Hong, B. H. (2012). Anomalous Behaviors of Visible Luminescence from Graphene Quantum Dots: Interplay between Size and Shape. *ACS Nano*, *6*(9), 8203–8208. https://doi.org/10.1021/nn302878r

¹⁴ Wang, J., Mu, X., & Sun, M. (2019). The Thermal, Electrical and ThermoelectricProperties of Graphene Nanomaterials. *Nanomaterials (Basel, Switzerland)*, *9*(2), 218. <u>https://doi.org/10.3390/nano9020218</u>

¹⁵ Leconte, N., Moser, J., Ordejón, P., Tao, H., Lherbier, A., Bachtold, A., Alsina, F., Sotomayor Torres, C. M., Charlier, J.-C., & Roche, S. (2010). Damaging Graphene with Ozone Treatment: A Chemically Tunable Metal–Insulator Transition. *ACS Nano*, *4*(7), 4033–4038. <u>https://doi.org/10.1021/nn100537z</u>

¹⁶ Yong, X., Nagaraja, T., Krishnamoorthy, R., Guanes, A., Das, S. R., & Martsinovich, N. (2023). Theoretical and Experimental Studies of Molecular Interactions between Engineered Graphene and Phosphate Ions for Graphene-Based Phosphate Sensing. *ACS Applied Nano Materials*. <u>https://doi.org/10.1021/acsanm.3c04147</u>

¹⁷ Tiwari, S. K., Sahoo, S., Wang, N., & Huczko, A. (2020). Graphene research and their outputs: Status and prospect. *Journal of Science: Advanced Materials and Devices*, 5(1). https://doi.org/10.1016/j.jsamd.2020.01.006

¹⁸ Smith, A. T., LaChance, A. M., Zeng, S., Liu, B., & Sun, L. (2019). Synthesis, properties, and applications of graphene oxide/reduced graphene oxide and their nanocomposites. *Nano Materials Science*, 1(1), 31–47. https://doi.org/10.1016/j.nanoms.2019.02.004

¹⁹ Afshari, F., & Ghaffarian, M. (2017). Electronic properties of zigzag and armchair graphene nanoribbons in the external electric and magnetic fields. *Physica E: Low-Dimensional Systems and Nanostructures*, *89*, 86–92. <u>https://doi.org/10.1016/j.physe.2017.02.007</u>

²⁰ Majumder, S., Meher, A., Srikanta Moharana, & Ki Hyeon Kim. (2024). Graphene nanoribbon synthesis and properties in polymer composites: A review. *Carbon*, *216*, 118558–118558. https://doi.org/10.1016/j.carbon.2023.118558

²¹ Wakabayashi, K. (2011). Electronic Properties of Graphene Nanoribbons. *Nanoscience and Technology*, 277–299. https://doi.org/10.1007/978-3-642-22984-8_9

²² Warner, J. H., Schaffel, F., Rummeli, M., & Alicja Bachmatiuk. (2013). *Graphene : fundamentals to applications*. Kidlington, Oxford: Elsevier.

²³ Muh. Yusrul Hanna, Santoso, I., & Moh. (2018). The Role of the Oxygen Impurity on the Electronic Properties of Monolayer Graphene: A Density-Functional Study. *Journal of Physics*, *1011*, 012071–012071. https://doi.org/10.1088/1742-6596/1011/1/012071

²⁴ Nakada, K., Fujita, M., Dresselhaus, G., & Dresselhaus, M. S. (1996). Edge state in graphene ribbons: Nanometer size effect and edge shape dependence. *Physical Review B*, *54*(24), 17954–17961. https://doi.org/10.1103/physrevb.54.17954

²⁵ Yu, S.-S., Wang, C., Zheng, W.-T., & Jiang, Q. (2011). Mechanical and electron-transport properties of graphene nanoribbons under tensile strain: A first-principles study. *Physica Status Solidi (A), 208*(10), 2328–2331. <u>https://doi.org/10.1002/pssa.201084168</u>

²⁶ Wagner, P., Ewels, C. P., Jean Joseph Adjizian, Magaud, L., Pascal Pochet, Roche, S., López-Bezanilla, A., Ivanovskaya, V. V., Yaya, A., Rayson, M., P.R. Briddon, & Humbert, B. (2013). Band Gap Engineering via Edge-Functionalization of Graphene Nanoribbons. *Journal of Physical Chemistry C*, *117*(50), 26790–26796. https://doi.org/10.1021/jp408695c

²⁷ Martin-Martinez, F. J., Fias, S., Van Lier, G., De Proft, F., & Geerlings, P. (2013). Tuning aromaticity patterns and electronic properties of armchair graphene nanoribbons with chemical edge functionalisation. *Physical Chemistry Chemical Physics*, *15*(30), 12637. <u>https://doi.org/10.1039/c3cp51293b</u>

²⁸ Son, Y.-W., Cohen, M. L., & Louie, S. G. (2006). Energy Gaps in Graphene Nanoribbons. *Physical Review Letters*, *97*(21). <u>https://doi.org/10.1103/physrevlett.97.216803</u>

²⁹ Wassmann, T., Seitsonen, A. P., Saitta, A., Lazzeri, M., & Mauri, F. (2008). Structure, Stability, Edge States, and
 Aromaticity of Graphene Ribbons. *Physical Review Letters*, 101(9).
 <u>https://doi.org/10.1103/physrevlett.101.096402</u>

³⁰ Koskinen, P., Malola, S., & Häkkinen, H. (2008). Self-Passivating Edge Reconstructions of Graphene. *Physical Review Letters*, *101*(11). <u>https://doi.org/10.1103/physrevlett.101.115502</u>

³¹ Liu, L., Zhang, J., Gao, H., Wang, L., Jiang, X., & Zhao, J. (2016). Tailoring physical properties of graphene: Effects of hydrogenation, oxidation, and grain boundaries by atomistic simulations. *Computational Materials Science*, *112*, 527–546. <u>https://doi.org/10.1016/j.commatsci.2015.06.032</u>

³² Tran, T. T., Vu, T. C., Hoang, H. V., Huang, W.-F., Pham, H. T., & Minh, H. (2022). How are Hydroxyl Groups Localized on a Graphene Sheet? *ACS Omega*, *7*(42), 37221–37228. <u>https://doi.org/10.1021/acsomega.2c03447</u>

³³ Lee, S. M., Lee, Y. H., Hwang, Y. G., Hahn, J. R., & Kang, H. (1999). Defect-Induced Oxidation of Graphite. *Physical Review Letters*, 82(1), 217–220. https://doi.org/10.1103/physrevlett.82.217

³⁴ A. Allouche, & Ferro, Y. (2006). Dissociative adsorption of small molecules at vacancies on the graphite (0001) surface. *Carbon*, 44(15), 3320–3327. <u>https://doi.org/10.1016/j.carbon.2006.06.014</u>

³⁵ Carlsson, J. M., Hanke, F., Suljo Linic, & Scheffler, M. (2009). Two-Step Mechanism for Low-Temperature Oxidation of Vacancies in Graphene. *Physical Review Letters*, *102*(16). <u>https://doi.org/10.1103/physrevlett.102.166104</u>

³⁶ Hofer, C., Skákalová, V., Görlich, T., Tripathi, M., Mittelberger, A., Mangler, C., Monazam, M. R. A., Susi, T., Kotakoski, J., & Meyer, J. C. (2019). Direct imaging of light-element impurities in graphene reveals triple-coordinated oxygen. *Nature Communications*, *10*(1). <u>https://doi.org/10.1038/s41467-019-12537-3</u>

³⁷ David, Galbiati, M., de, D., Sahalianov, I. Y., Radchenko, T. M., Sun, J., Peña, D., Lene Gammelgaard, Jessen, B. S., Thomsen, J. D., Bøggild, P., Aran Garcia-Lekue, Camilli, L., & Caridad, J. M. (2021). Unraveling the electronic properties of graphene with substitutional oxygen. *2D Materials*, *8*(4), 045035–045035. https://doi.org/10.1088/2053-1583/ac28ab

³⁸ Amirhasan Nourbakhsh, Mirco Cantoro, Vosch, T., Pourtois, G., Clemente, F., Marleen, Johan Hofkens, Heyns, M., Stefan De Gendt, & Sels, B. F. (2010). *Bandgap opening in oxygen plasma-treated graphene*. *21*(43), 435203–435203. <u>https://doi.org/10.1088/0957-4484/21/43/435203</u>

³⁹ Kozbial, A., Zhou, F., Li, Z., Liu, H., & Li, L. (2016). Are Graphitic Surfaces Hydrophobic? Accounts of Chemical Research, 49(12), 2765–2773. <u>https://doi.org/10.1021/acs.accounts.6b00447</u>
 ⁴⁰ Banhart, F., Kotakoski, J., & Krasheninnikov, A. V. (2010). Structural Defects in Graphene. ACS Nano, 5(1), 26–41. <u>https://doi.org/10.1021/nn102598m</u>

⁴¹ El-Barbary, A. A., Telling, R., Ewels, C. P., Heggie, M. I., & Briddon, P. R. (2003). Structure and energetics of the vacancy in graphite. *Physical Review*, *68*(14). <u>https://doi.org/10.1103/physrevb.68.144107</u>

6. A Comparative Analysis of Experimental and Computational Results on Graphene-Based Materials

CONTENTS

List of Figures	237
5.1. Comparison and Evaluation of Experimental and Computational Optical Absorbance Results .	238
6.1.1. Optical Properties	238
6.1.1.1. The Influence of Morphology on the Optical Properties of Graphene Derivatives	238
6.1.1.2. Impact of Oxygen Functionalisation on the Optical Properties of Graphene	239
6.1.1.3. The Influence of Defects on the Optical Properties of Graphene	241
6.2. Trap States	243
5.3. References	245

LIST OF FIGURES

Figure 6.1. (a, b) Comparison of Experimental Absorbance Spectra for Pristine Graphene (black lines) and AG (coloured lines). Compared to pristine graphene, the normalised absorbance spectra in (b) clearly demonstrate a broadening effect in Aerogel graphene samples. (c, d) Theoretical calculations of Graphene and AG with Varying Degrees of Zigzag Curvature support the experimental observations.

Figure 6.2. Normalised Experimental (black line) and Calculated (red line) Absorbance Spectra of Graphene, Showing Agreement Between the Two. The calculated spectrum exhibits non-zero absorbance at longer wavelengths and a slightly narrower peak than the experimental spectrum.

Figure 6.3. The Calculated Absorbance Spectra Demonstrate the Influence of Different Oxygen Functional Groups on the Absorption Profile of Graphene. The Coloured Lines Represent Various Oxygen Functionalisation.

Figure 6.4. The Experimental Normalised Absorbance Spectra Show Pristine Graphene in Black. The Coloured Lines Represent Aerogel Graphene Samples with Varying Degrees of Oxygen Content.

Figure 6.5. Calculated Absorbance Spectra for Pristine Graphene (black), Graphene with a Stone-Wales (SW) Defect (red), and Graphene with a Monovacancy (blue).

Figure 6.6. Experimental UV-Vis Absorbance Spectra of Pristine Graphene (black) and Graphene Aerogels (AG 0.4 in blue, AG 0.5 in pink)

Figure 6.7. Band Structures and Atomic Configurations of Pristine Graphene (left), Graphene with an Oxygen Substitution Group (middle), and Graphene with 20% Curvature (right).

A Comparative Analysis of Experimental and Computational Results on Graphene-Based Materials

6.1. COMPARISON AND EVALUATION OF EXPERIMENTAL AND COMPUTATIONAL OPTICAL ABSORBANCE RESULTS

To gain a comprehensive understanding of how the atomic structure affects the optical properties of graphene derivatives, it was essential to compare the experimental absorbance spectra with computational models. Absorption spectra serve as an essential part of material characterisation, and they can be theoretically modelled to provide insight into the electronic transitions occurring within the material.

6.1.1. Optical Properties

6.1.1.1. The Influence of Morphology on the Optical Properties of Graphene Derivatives Figure 6.1 (a) and (b) illustrate the measured absorbance spectra of pristine graphene, represented by black lines, and the measured spectra of graphene aerosol gels (AG), represented by coloured lines, alongside their theoretical counterparts for flat and curved graphene structures in Figure 6.1 (c) and (d). As presented in Figure 6.1 (b), the normalised absorbance data for the AG samples reveals a pronounced broadening effect. This broadening, which has been discussed comprehensively in Chapter 4, is likely attributable to the heterogeneous particle sizes present within the AG samples. In contrast, pristine graphene exhibits a more uniform sheet-like structure. This difference in morphology results in distinct optical properties.



Figure 6.1. (a, b) Comparison of Experimental Absorbance Spectra for Pristine Graphene (black lines) and AG (coloured lines). Compared to pristine graphene, the normalised absorbance spectra in (b) clearly demonstrate a broadening effect in Aerogel graphene samples. (c, d) Theoretical calculations of Graphene and AG with Varying Degrees of Zigzag Curvature support the experimental observations.

The transmission electron microscopy (TEM) findings discussed in Chapter 4 offer valuable insights into the morphology of particles, revealing a diverse range of curved, bent, and crumpled structures within the graphene lattice. These variations in morphology are likely to be accountable for the differences observed in absorbance profiles.

The primary absorbance peak for graphene, attributed to the π - π * transitions, is observed experimentally at ~ 270 nm. In the theoretical calculations depicted in Figure 6.1 (c), the corresponding peak appears at around 300 nm, this is also depicted in Figure 6.2. This shift in the peak position can be attributed to the computational methods used in the calculations of the spectra. These calculations used the vdW-DF2 functional¹, which is a semi-local exchange-correlation functional with non-local correlation. This functional, like GGA-type semi-local functionals, is expected to underestimate band gaps, and therefore calculated spectra are expected to be red-shifted. The theoretical calculations, as shown in the zoomed-in representation in Figure 6.1 (d), substantiate the hypothesis that curvature significantly contributes to spectral broadening. While the curvature illustrated in the theoretical structures is relatively small compared to the pronounced shapes observed in the AG samples, it nonetheless supports the experimental findings regarding the spectral broadening phenomena.



Figure 6.2. Normalised Experimental (black line) and Calculated (red line) Absorbance Spectra of Graphene, Showing Agreement Between the Two. The calculated spectrum exhibits non-zero absorbance at longer wavelengths and a slightly narrower peak than the experimental spectrum.

6.1.1.2. Impact of Oxygen Functionalisation on the Optical Properties of Graphene

Theoretical studies of oxygen-containing graphene in chapter 5 reveal that oxygen functionalisation induces significant changes in the optical properties of graphene. Figure 6.3 illustrates the calculated absorbance spectra, showcasing the influence of various types of oxygen functional groups, including epoxide, hydroxyl, and oxygen substitution, on the absorption profile of graphene. These modifications result in decreased absorbance and a more pronounced broadening with oxygen functionalisation, compared to the pure graphene peak at approximately 300 nm.



Figure 6.3. The Calculated Absorbance Spectra Demonstrate the Influence of Different Oxygen Functional Groups on the Absorption Profile of Graphene. The Coloured Lines Represent Various Oxygen Functionalisation.

In the experimental AG samples, the oxygen content ranged from AG 0.3 to AG 0.75. This set of samples enabled us to investigate the effect of the oxygen content on optical absorption properties. In the experimental analysis, the examination of oxidised graphene spectra demonstrates a systematic broadening of the absorption spectra with increased oxygen content. Figure 6.4, which corresponds to the same data as Figure 6.1 (b), illustrates the absorbance spectra of pristine graphene (in black) and oxidised graphene aerogels (coloured lines) and reveals broadening effects following oxidation. This is consistent with the theoretical prediction that the introduction of oxygen should induce modifications to the electronic structure of graphene, leading to changes in its optical properties, such as the broadening of the main absorption peak, as detailed in Chapter 5. This broadening effect serves to confirm the significant role of oxygen functionalisation in the absorbance profile of graphene, as observed in both the experimental and theoretical contexts.



Figure 6.4. The Experimental Normalised Absorbance Spectra Show Pristine Graphene in Black. The Coloured Lines Represent Aerogel Graphene Samples with Varying Degrees of Oxygen Content.

6.1.1.3. The Influence of Defects on the Optical Properties of Graphene

Our theoretical investigations have also demonstrated the significant impact of defects on the optical absorbance of graphene. In Figure 6.5, the calculated absorbance spectra for pristine graphene (black) and graphene featuring specific defects, such as graphene with the Stone-Wales (SW) defect (red) and a monovacancy (blue) are presented. The presence of the SW defect results in a distinct peak at a similar wavelength as pristine graphene, however with reduced intensity, highlighting a small change to the electronic states due to the defect. Conversely, the monovacancy produces a double peak, slightly shifted from the absorbance of pristine graphene and graphene with SW defects, emphasising the different electronic perturbations associated with each defect type.



Figure 6.5. Calculated Absorbance Spectra for Pristine Graphene (black), Graphene with a Stone-Wales (SW) Defect (red), and Graphene with a Monovacancy (blue).

Based on experimental observations, the AG samples (AG 0.3 - AG 0.75 shown in Figure 6.4 and AG 0.4 and AG 0.5 shown in Figure 6.6) exhibit significant broadening in their absorbance spectra, which can be attributed to the presence of structural defects as well as the presence of oxygen groups. Analysis of scanning electron microscopy (SEM) and TEM images in chapter 4.3 reveals that AG 0.4 consists of smaller particle sizes and a crumpled nanosheet structure, while AG 0.5 demonstrates more pronounced curvature with possible nano-shell formations. These observed morphological disparities between AG 0.4 and AG 0.5 may be linked to defects such as vacancies or Stone-Wales defects. As illustrated in Figure 6.6, the absorbance spectra for both AG samples, compared to pristine graphene, exhibit noticeable broadening and slight redshifts. Pristine graphene (black line) displays the characteristic peak attributed to π - π * electronic transitions, while the AG samples display a red shift of this peak, indicating alterations in graphene's electronic structure. The observed red shift,

combined with theoretical predictions shown in Figure 6.5, suggests the plausible presence of defects like monovacancies in the experimental samples.



Figure 6.6. Experimental UV-Vis Absorbance Spectra of Pristine Graphene (black) and Graphene Aerogels (AG 0.4 in blue, AG 0.5 in pink)

Theoretical results provide deeper insight into how different defects modify graphene's absorbance profile by forming new electronic states as discussed in Chapter 5. Defects broaden and shift the absorbance peaks, significantly impacting graphene's optical properties. The agreement between trends seen in the experimental and theoretical results suggests the likelihood that AG samples contain a mixture of various defects.

6.2. Trap States

There is evidence of trap states in AG samples as observed through transient absorption spectroscopy (TAS) in Chapter 4, where oxygen functionalisation significantly influences carrier recombination dynamics. Specifically, AG films with a higher oxygen content exhibit extended carrier lifetimes, which can be attributed to localised trap states. Since the presence of functional groups containing oxygen, such as hydroxyl and carbonyl, is demonstrated by X-ray photoelectron spectroscopy (XPS) and Fourier-transform infrared spectroscopy (FTIR), it can be hypothesised that the introduction of oxygen functional groups in the AG samples studied throughout this work is responsible for the formation of localised trap states and delocalised states is critical to explaining the electronic behaviour observed in oxygen-functionalized AG films. Trap states in the band structure are represented by nearly flat energy bands, indicating minimal energy variation with respect to

momentum (k-points). The limited dispersion of these bands indicates highly localised electronic states, restricting charge carriers, such as electrons or holes, to specific regions of the material, thereby impeding their mobility. These states often result from lattice disruptions, such as defects induced by oxygen functionalisation, which act as barriers to carrier mobility. Conversely, delocalised states are characterised by bands with significant dispersion, where energy levels vary substantially with momentum. In these states, charge carriers can freely traverse the material, leading to enhanced mobility and electrical conductivity. Presence of localised states arising from particular atomic structures can be revealed using DFT calculations.

The band structure of pristine graphene, shown in Figure 6.7 (left panel), displays the characteristic linear dispersion near the Fermi level, where the Dirac cones emerge. This indicates the presence of massless Dirac fermions, which are fully delocalised throughout the material. The absence of flat bands near the Fermi level confirms that no trap states exist in pristine graphene, consistent with its high electrical conductivity and mobility. The electronic states are free to move across the material, unhindered by the presence of defects or structural deformations.



Figure 6.7. Band Structures and Atomic Configurations of Pristine Graphene (left), Graphene with an Oxygen Substitution Group (middle), and Graphene with 20% Curvature (right).
The middle panel of Figure 6.7 presents the band structure of graphene with a single oxygen substitution atom, where a nearly flat band appears below the Fermi level. This flat band is indicative of localised hole states, also referred to as trap states. The disruption of the electronic structure caused by the substitutional oxygen leads to the formation of a localised energy level, which confines charge carriers. This is in direct alignment with the findings of TAS, which suggest that the presence of oxygen introduces localised trap states that prolong carrier recombination times by reducing carrier mobility. The calculations reveal that these hole trap states arise as a result of oxygen-related defects disrupting the otherwise delocalised electronic structure of graphene.

Furthermore, Figure 6.7 (right panel) reveals the impact of curvature on the band structure, particularly in graphene with 20% curvature along the zigzag direction. The partial flattening of bands along the Γ -P-X direction indicates localised states in the x-direction (zigzag direction), while these states remain delocalised the y-direction (armchair direction). This anisotropic behaviour, induced by curvature, suggests that the structural strain from bending modifies the periodic potential of the graphene lattice. Such curvature-induced strain leads to spatial confinement of carriers in one dimension while allowing greater mobility in another.

In summary, AG films, which can be described as graphene with structural and chemical modifications, exhibit delayed carrier dynamics due to these modifications. The oxygen functional groups, such as those introduced via oxygen substitution, are likely responsible for creating localised trap states. This is corroborated by the band structure analysis in Figure 6.7, which demonstrates that oxygen substitution can lead to significant carrier trapping, while curvature appears to have a smaller effect on carrier mobility. Thus, the presence of curvature and chemical changes arising from oxygen incorporation in the AG films play a fundamental role in modulating their electronic properties, in particular by facilitating the formation of trapped states.

6.3. REFERENCES

¹ Lee, K., Murray, É. D., Kong, L., Lundqvist, B. I., & Langreth, D. C. (2010). Higher-accuracy van der Waals density functional. *Physical Review B*, *82*(8). <u>https://doi.org/10.1103/physrevb.82.081101</u>

7. Conclusion

CONTENTS

Overview	.248
7.1. Summary of Experimental Findings	.249
7.2. Summary of Theoretical Findings on Oxygen Functionalization and Curvature	.250
7.3. Combined Summary of Experimental and Theoretical Findings	.251
7.4. Technological Implications	.252
7.4.1. Potential of Graphene-Based Phosphate Sensors in Smart Farming	.252
7.5. The SITS Project Journey	.253
7.5.1. SitS Sensor Device	.253
7.7. References	.254

Conclusion

OVERVIEW

This thesis has comprehensively investigated the multifaceted influence of oxygen functionalisation and structural modifications, such as curvature and defects, on graphene's electronic and optical properties through graphene aerogel films and functionalised graphene structures. Through a combination of ultrafast transient absorption spectroscopy, characterisation techniques such as electron microscopy, and density functional theory calculations, this research offers an interconnected and comprehensive outline for understanding how variations in oxygen content and structural deformation impact the physical and chemical behaviour of these carbon-based materials. The results not only enhance our understanding of graphene's inherent properties but also present opportunities for customising these properties to align with the specific requirements of advanced applications in electronics, optoelectronics, and sensing technologies.

7.1. SUMMARY OF EXPERIMENTAL FINDINGS

The research detailed in this thesis investigates the impact of oxygen on the structural properties and charge carrier dynamics of AG films. Through the use of transient absorption spectroscopy, the study reveals that oxygen functional groups play a significant role in influencing carrier recombination times by introducing localised trap states, thereby prolonging carrier lifetimes. Specifically, AG films with higher oxygen content exhibit extended carrier lifetimes, which can be attributed to the presence of hydroxyl and carbonyl groups, as confirmed through X-ray photoelectron spectroscopy and Fourier-transform infrared spectroscopy.

The observed increase in carrier lifetime indicates potential applications of oxygen-functionalized AG in devices requiring charge storage and extended carrier dynamics. This study demonstrates that oxygen functionalisation can introduce trap states into graphene, thereby altering its electrical conductivity and overall relaxation behaviour. Our research findings emphasise that oxygen functionalisation not only introduces defects but also leads to a complex redistribution of electronic states, enhancing specific properties based on the intended application.

Additionally, analysis conducted with scanning electron microscopy and transmission electron microscopy has demonstrated that the morphology of AG films is significantly altered by the incorporation of oxygen. The presence of oxygen results in stacking disorder, disrupting the regularity of the graphene lattice and leading to an increase in particle size. These changes in morphology are strongly associated with shifts in the electronic and optical properties of AG.

7.2. SUMMARY OF THEORETICAL FINDINGS ON OXYGEN FUNCTIONALIZATION AND CURVATURE

Our calculations presented in this thesis show that the electronic structure of graphene can be effectively modified through oxygen functionalisation, as elucidated by theoretical calculations using Density Functional Theory. Our results demonstrate that the introduction of oxygen groups disrupts the electronic structure of graphene, leading to the formation of a customisable bandgap. This bandgap widening occurs because oxygen defects segment the continuous graphene lattice into smaller regions resembling graphene nanoribbons. The arrangement of oxygen atoms is crucial; when defects are further apart, the resulting nanoribbon-like sections become narrower, leading to an increased bandgap.

Additionally, substitutional oxygen atoms introduce lattice strain, which alters local electronic properties and leads to the formation of trap states for electrons and holes. Therefore, understanding and controlling the oxygen content and defect positioning is key to optimising graphene's electronic properties for applications such as sensors.

Furthermore, this research explores how curvature influences graphene's electronic properties. Highly curved regions experience compressive strain, which shortens carbon-carbon bond lengths and leads to localised electronic states in the conduction band. In these strained regions, bond lengths decrease from the typical graphene bond length (~1.42 Å) to approximately 1.408 to 1.418 Å, enhancing reactivity. These strained areas present favourable sites for chemical modifications and catalytic reactions, which could benefit future sensor and catalysis applications.

7.3. COMBINED SUMMARY OF EXPERIMENTAL AND THEORETICAL FINDINGS

The combination of experimental and theoretical methodologies provides a thorough understanding of the impact of oxygen functionalisation and structural changes on graphene's properties. Experimental findings demonstrated that oxygen functional groups introduce trap states that delay carrier recombination, while theoretical analyses have revealed their ability to create a customisable bandgap, significantly altering the electronic structure of graphene. Theoretical results from this study also suggest substitutional oxygen as a cause for trap states. Additionally, the optical absorption spectra obtained during this investigation, both experimentally and computationally, demonstrated a redshift in the π - π * transition peak in oxygen-functionalised graphene, accompanied by peak broadening and the emergence of shoulder peaks.

Furthermore, the structural distortions caused by oxygen functionalisation may induce ripples and out-of-plane deformations in the graphene lattice. These localised ripples result from the strain introduced by oxygen groups. The theoretical findings suggest that these curvature-induced localised states could enhance graphene's sensitivity to environmental changes, making it particularly suitable for sensing applications.

These findings suggest that precise management of oxygen content, placement, and curvature offers a novel strategy for enhancing graphene for next-generation sensors and other technologies.

7.4. TECHNOLOGICAL IMPLICATIONS

This thesis presents evidence indicating that oxygen-functionalised and structurally modified graphene provide a means of tuning of graphene's electronic structure. Thanks to this tunability of properties, functionalised graphene can serve as a platform for a wide range of technological innovations. The ability to introduce a tunable bandgap through oxygen doping enables graphene to be adapted for semiconductor applications. In contrast to pristine graphene, which lacks a bandgap and is therefore unsuitable for most electronic devices, oxygen-functionalised graphene can be utilised in the development of transistors, photodetectors, and other electronic devices that necessitate precise regulation of carrier mobility and conductivity.¹⁻²

Incorporating curvature into graphene structures presents additional opportunities for enhancing graphene's electronic and mechanical properties. Strain-engineered graphene could play a crucial role in the development of flexible electronics or sensors that require mechanical flexibility without sacrificing electronic performance.

7.4.1. Potential of Graphene-Based Phosphate Sensors in Smart Farming

The conclusions drawn from this thesis transcend basic research and offer valuable insights into the practical use of graphene for developing phosphate sensors in the context of smart farming. Given the increasing importance of precision agriculture in ensuring sustainable food production, the real-time monitoring of soil nutrients, particularly phosphates, has become a critical necessity. Phosphorus, an essential nutrient for plant growth, requires accurate monitoring and management to optimise crop yields and reduce environmental pollution resulting from over-fertilization.

The structural and electronic modifications of graphene, such as oxygen functionalisation and curvature-induced strain, present promising opportunities for increasing the material's sensitivity to phosphate ions.³

The presence of oxygen functional groups, which serve as reactive adsorption sites, has been shown to facilitate the binding of phosphate ions, as evidenced by recent research in our group.³ The localised ripples surrounding oxygen functional groups play a significant role in enhancing the interaction between graphene and phosphate ions, making oxygen-functionalized graphene an excellent candidate for phosphate sensors. Furthermore, pristine, oxygen-functionalised and curved graphene were found to display distinct trends in conductivity upon adsorption of phosphate.³ This is particularly advantageous for the detection of low concentrations of phosphates in soil, which is crucial for precision agriculture.

Integration of graphene-based phosphate sensors into existing platforms, such as IoT systems, could provide farmers with real-time data on soil nutrient levels, enabling more efficient and precise fertiliser application. The existing platforms, such as IoT-based monitoring systems, have demonstrated their ability to improve agricultural productivity through the continuous collection and analysis of data related to essential soil nutrients, moisture levels, and pH. This process allows for the optimization of resource utilization and contributes to enhanced crop yields.⁴

7.5. THE SITS PROJECT JOURNEY

The latest developments regarding the Signals in the Soils (SitS) Project can be found in the Appendix.

7.5.1. SitS Sensor Device

The recent progress in the SitS project has underlined the potential of sensor technology, particularly with the incorporation of graphene as an electrode material. While the research in this thesis has demonstrated the successful functionalisation of graphene to improve its electrochemical properties, it is important to acknowledge that modifying the properties of graphene alone may not achieve the highest sensitivity and selectivity necessary for practical and effective sensing applications.⁵

Emerging findings indicate that a hybrid approach involving the combination of graphene with complementary materials, such as metal nanoparticles or conductive polymers, can significantly improve sensor performance. This approach leverages the unique properties of each material to establish a more resilient and efficient sensing platform.⁶

The recent progress of the SitS project has led to the development of an innovative sensor device that employs the distinctive properties of graphene as an electrode material. This sensor integrates highquality, atomically thin, and nanoscale-controlled carbon materials, augmenting its electrochemical, physical, and chemical attributes. Moreover, the design incorporates additive manufacturing techniques, showcasing the potential for heightened sensitivity and selectivity in detecting soil phosphorus dynamics. However, exclusive reliance on graphene modification may prove inadequate in achieving the desired performance for sensing applications. By integrating graphene with complementary materials such as metal nanoparticles and conductive polymers, the SitS sensor aims to surmount these challenges and establish a robust framework for environmental monitoring, particularly in nutrient management in agricultural systems.

7.7. REFERENCES

¹ Radsar, T., Khalesi, H., & Ghods, V. (2021). Graphene properties and applications in nanoelectronic. *Optical and Quantum Electronics*, *53*(4). <u>https://doi.org/10.1007/s11082-021-02839-6</u>

² Zhu, X., Liu, K., Lu, Z., Xu, Y., Qi, S., & Zhang, G. (2020). Effect of oxygen atoms on graphene: Adsorption and doping. *Physica E: Low-Dimensional Systems and Nanostructures*, *117*, 113827. https://doi.org/10.1016/j.physe.2019.113827

³ Yong, X., Nagaraja, T., Krishnamoorthy, R., Guanes, A., Das, S. R., & Martsinovich, N. (2023). Theoretical and Experimental Studies of Molecular Interactions between Engineered Graphene and Phosphate Ions for Graphene-Based Phosphate Sensing. *ACS Applied Nano Materials*. <u>https://doi.org/10.1021/acsanm.3c04147</u>

⁴ Senapaty, M. K., Ray, A., & Padhy, N. (2023). IoT-Enabled Soil Nutrient Analysis and Crop Recommendation Model for Precision Agriculture. *Computers*, *12*(3), 61. <u>https://doi.org/10.3390/computers12030061</u>

⁵ Sainz-Urruela, C., Vera, S., San, P., & Díez-Pascual, A. M. (2021). *Graphene-Based Sensors for the Detection of Bioactive Compounds: A Review*. 22(7), 3316–3316. <u>https://doi.org/10.3390/ijms22073316</u>

⁶ Graphene-supported nanomaterials as electrochemical sensors: A mini review. (2021). *Results in Chemistry*, *3*, 100131. <u>https://doi.org/10.1016/j.rechem.2021.100131</u>

8. Future Work

CONTENTS

8.1. Experimental Future Work	257
8.1.1. Advanced Spectroscopic Techniques: Terahertz	257
8.1.2. High-Resolution Microscopy: STEM	257
8.1.3. High-Resolution Microscopy: STM	257
8.1.4. High-Resolution Microscopy: TEM, EELS technique	257
8.1.5. Alternative Heteroatoms and Functional Groups	258
8.2. Computational Future Directions	259
8.2.1. Simulations of XPS spectra	259
8.2.2. More Complex Geometries	259
8.3. References	

Future Work

8.1. EXPERIMENTAL FUTURE WORK

This study has illustrated the substantial influence of oxygen content on the optoelectronic characteristics of the novel graphene aerogel materials and has presented potential avenues for future investigations. While the findings presented in this research establish the groundwork for comprehending these materials, there are still numerous aspects to be investigated more deeply in order to fully understand their capabilities, particularly in sensor applications.

8.1.1. Advanced Spectroscopic Techniques: Terahertz

One potentially valuable direction for future investigation involves employing advanced optical-pump terahertz-probe spectroscopy. This approach has the potential to facilitate the real-time monitoring of carrier dynamics in oxygen-functionalised graphene aerogels.¹ By examining electron mobility and recombination rates in the presence of oxygen, this method may yield critical insights into how oxygen levels affect the electronic properties of these materials.

8.1.2. High-Resolution Microscopy: STEM

Scanning transmission electron microscopy (STEM) is a useful technique for future exploration. With its enhanced spatial resolution, STEM has the capability to map the distribution of oxygen atoms with high accuracy within the graphene aerogel structure.² This mapping would provide valuable insights into the impact of oxygen on local conductivity and the overall structural integrity of the material. Such understanding would be essential for optimising graphene's performance in electronic devices and sensors.

8.1.3. High-Resolution Microscopy: STM

Scanning tunnelling microscopy (STM) is an effective technique that complements STEM in the highresolution examination of graphene's atomic structure and electronic properties. Unlike STEM, which provides spatial mapping using transmitted electrons, STM enables visualisation at atomic resolution by measuring the tunnelling current between a probe and the sample surface at specific energies relative to the Fermi level. This tunnelling current exposes the electronic states associated with defects, making STM particularly valuable for comprehending the electronic behaviour of oxygenfunctionalized graphene. By identifying variations in electronic states, STM offers detailed insights into how oxygen functional groups and defects impact local electronic properties.³ This capability is especially useful for optimising graphene's performance in electronic devices and sensors, where even minor alterations in electronic structure can have significant impacts.

8.1.4. High-Resolution Microscopy: TEM, EELS technique

This study attempted to use Electron Energy Loss Spectroscopy (EELS) during TEM analysis. Unfortunately, this research encountered technical difficulties that hindered data acquisition. However, it is important to revisit this analysis in future work, as EELS has the potential to provide valuable insights into various material properties. Specifically, it allows for precise detection and quantification of elemental composition, including oxygen and other heteroatoms, which are crucial for understanding material heterogeneity. EELS also offers information on chemical bonding, particularly regarding the oxidation states and bonding configurations between carbon and oxygen atoms, which would be very useful to identify the exact oxygen functional groups present in the AG samples to complement the XPS results. Additionally, it provides insights into the electronic structure by revealing details about the band structure, density of states, and Fermi level shifts. Furthermore, examining valence and core loss features through EELS enables a thorough investigation of local electronic excitations, which are essential for comprehending the optoelectronic properties of materials.⁴

Leveraging these insights would significantly enhance our understanding of how oxygen functionalisation impacts graphene, with direct implications for its use in applications such as sensing and electronic devices.

8.1.5. Alternative Heteroatoms and Functional Groups

The focus of this thesis has been primarily on the functionalisation by oxygen. However, it would be beneficial for future research to broaden this focus to include other heteroatoms, such as sulfur, nitrogen, and silicon, in the AG films. The introduction of these atoms has the potential to tailor the electronic properties of graphene, thereby leading to new functionalities, especially in sensing applications.⁵

8.2. COMPUTATIONAL FUTURE DIRECTIONS

8.2.1. Simulations of XPS spectra

It is crucial to simulate XPS spectra for the various oxygen-containing and defect-containing structures. Comparison between simulated and experimental XPS spectra would reveal the chemical environments of carbon atoms and would confirm the types of functional groups present in the experimental AG samples. Simulations of XPS spectra can be carried out using the Vienna Ab initio Simulation Package (VASP)⁶. For example, T. Susi et al.⁷ calculated core level binding energies using the delta Kohn–Sham total energy differences method with the GPAW software. Additionally, a study using VASP demonstrated the calculation of core-level shifts, which are measured in XPS.⁸ These simulations will facilitate a more precise understanding of the oxygen and graphene interactions. This investigation was intended but not attempted due to time limits.

8.2.2. More Complex Geometries

In future computational studies, it is important to direct attention towards the modelling of graphene aerogels and reduced graphene oxide (rGO) structures in configurations that are more representative of real-world scenarios, such as curved or flaked geometries. Given that natural graphene typically exists in flake-like forms and rGO exhibits a more disordered structure, simulating these configurations will offer a more precise understanding of graphene's behaviour in practical applications. For example, more extensive studies of combinations of curvature and functional groups, and multilayer curved graphene with functional groups, would offer better representation of realistic oxidised graphene aerogel structures.

8.3. REFERENCES

¹ Rane, S., Kothuru, A., Jana, A., Devi, K. M., Goel, S., Prabhu, S., & Roy Chowdhury, D. (2022). Broadband terahertz characterization of graphene oxide films fabricated on flexible substrates. *Optical Materials*, *125*, 112045. https://doi.org/10.1016/j.optmat.2022.112045

² Scanning Transmission Electron Microscopy - Nanoscience Instruments. (n.d.). https://www.nanoscience.com/techniques/scanning-transmission-electron-microscopy/

³ Nanoscience Instruments. (2018). *Scanning Tunneling Microscopy - Nanoscience Instruments*. Nanoscience Instruments. <u>https://www.nanoscience.com/techniques/scanning-tunneling-microscopy/</u>

⁴ Egerton, R. F. (2011). *Electron energy-loss spectroscopy in the electron microscope*. Springer.

⁵ Liu, H., Liu, Y., & Zhu, D. (2011). Chemical doping of graphene. *J. Mater. Chem.*, *21*(10), 3335–3345. https://doi.org/10.1039/c0jm02922j

⁶ Kresse, G., & Furthmüller, J. (1996). Efficient iterative schemes forab initiototal-energy calculations using a plane-wave basis set. *Physical Review B*, *54*(16), 11169–11186. <u>https://doi.org/10.1103/physrevb.54.11169</u>

⁷ Susi, T., Kaukonen, M., P. Havu, Ljungberg, M. P., Ayala, P., & Kauppinen, E. I. (2014). Core level binding energies of functionalized and defective graphene. *Beilstein Journal of Nanotechnology*, *5*, 121–132. https://doi.org/10.3762/bjnano.5.12

⁸ Köhler, L., & Kresse, G. (2004). Density functional study of CO on Rh(111). *Physical Review B*, 70(16). https://doi.org/10.1103/physrevb.70.165405 9. Additional Research Projects on Metal-oxides, Graphitic, and Molecular Materials Projects

CONTENTS

9.1. Expe	rimental Projects
9.1.1. Metals wi	Optical Properties of TiO ₂ Nanoparticles Decorated with Nanoclusters of Different th Varying Nanoparticle Sizes (Project 1)
9.1.2. (Project Ty	Optical Properties of TiO ₂ Nanoparticles with Metal Atoms with Varying Particle Sizes wo)
9.1.3. (Project T	Optical Properties of TiO_2 Nanoparticles with Metal Atoms with Varying Particle Sizes Three)
9.1.4.	Optical Properties of Quinoline and 1,10-Phenanthroline Derivatives
9.2. Theo	ry projects
9.2.1. Nanotube	Theoretical Calculations of Carbon Nanotubes and Oxygen-Functionalised Carbon s266
9.2.2.	Computational Investigation of Graphitic Carbon Nitride
9.2.3.	Theoretical Calculations of Quinoline and 1,10-Phenanthroline Derivatives266
9.3. Refer	rences

Additional Research Projects on Metal-oxides, Graphitic, and Molecular Materials Projects

This section concisely outlines additional research projects that were undertaken alongside my doctoral studies.

9.1. EXPERIMENTAL PROJECTS

9.1.1. Optical Properties of TiO₂ Nanoparticles Decorated with Nanoclusters of Different Metals with Varying Nanoparticle Sizes (Project 1)

Collaborator: Rosie Ma (The University of Sheffield - Department of Chemical Engineering) I assisted in Rosie Ma's PhD research at the Department of Chemical Engineering by conducting an analysis of the optical properties of TiO_2 samples. This analysis involved estimating Tauc plots for TiO_2 nanoparticles with varying diameters and samples doped with different metals and exhibiting a range of particle sizes. The characterisation process utilised UV-Vis¹ absorbance spectroscopy to determine the bandgap energies through Tauc plot analysis.

9.1.2. Optical Properties of TiO₂ Nanoparticles with Metal Atoms with Varying Particle Sizes (Project Two)

Collaborator: Dr Arthur Graf (The University of Cardiff)

This study characterised TiO_2 samples with various adsorbed metal atoms and engineered to exhibit a range of particle sizes. Dr Arthur Graf at the University of Cardiff synthesised and provided these samples.

The powder samples were used to create thin films using two different deposition techniques: drop casting and hot dropping onto thin glass substrates. These methods were chosen to ensure that the films had an even distribution and the right thickness, essential for accurate spectroscopic analysis.

The optical properties of the TiO_2 -metal systems were characterised using UV-visible spectroscopy to analyse the films' absorbance spectra in both the ultraviolet and visible regions. Additionally, transient absorption spectroscopy² was employed to examine the excited-state dynamics of the TiO_2 -metal systems.

9.1.3. Optical Properties of TiO₂ Nanoparticles with Metal Atoms with Varying Particle Sizes (Project Three)

Collaborator: Dr A. Lanterna (The University of Nottingham)

In this project, TiO₂-metal samples were received from Dr. Lanterna's research group at the University of Nottingham. These samples were similar to those described in sections 9.1.1 and 9.1.2, with the primary distinction being a broader range of particle sizes.

The samples were prepared into thin films using the same deposition techniques as previously employed. Comprehensive optical characterisation was conducted on these film samples, utilising UV-Vis spectroscopy to measure their absorbance across the ultraviolet and visible spectra. Additionally, transient absorption spectroscopy was performed to study these materials' excited-state dynamics and charge transfer processes. The broader range of particle sizes in these samples provided an opportunity to explore further the relationship between particle size distribution and the photophysical behaviour of the TiO₂ complexes.

9.1.4. Optical Properties of Quinoline and 1,10-Phenanthroline Derivatives

Collaborator: Dr Jacek Nycz (University of Silesia, Katowice, Poland)

UV-Vis spectroscopy was performed on quinoline and 1,10-phenanthroline derivatives to study their excited-state intramolecular proton transfer (ESIPT) properties. These chromophores are of interest due to their potential applications in various fields, such as UV stabilizers and fluorescence sensors. Additionally, I assisted Dr. Alex Auty with the initial transient absorption experiments to explore the excited-state dynamics of these samples.

9.2. THEORY PROJECTS

9.2.1. Theoretical Calculations of Carbon Nanotubes and Oxygen-Functionalised Carbon Nanotubes

This project studied the electronic and structural properties of different carbon nanotube configurations and their oxygen-functionalized derivatives. The calculations focused on three types of single-walled carbon nanotubes: chiral, zigzag, and armchair. For each type, the pristine nanotubes and those functionalised with an epoxide group and those with oxygen substitution were examined. This approach allowed for a detailed analysis of how these functional groups influence the electronic and structural properties of the nanotubes. The nanotubes' optical properties and band gaps were also studied. Preliminary results are presented in the Appendix section 10.5.

9.2.2. Computational Investigation of Graphitic Carbon Nitride

Collaborator: Dr Sayantan Bhattacharya and Dr Adam Clancy (Imperial College London) Gaussian³ software was used to model Poly-triazine imide (PTI), a precursor to $g-C_3N_4$, both with and without KBr. Subsequently, SIESTA⁴ software was employed to analyse the electronic structure and optical properties of $g-C_3N_4$ flakes and unit cells.

The investigation included analysing the optical absorption spectra of PTI to identify the electronic transitions responsible for light absorption. This analysis provided insights into how the $g-C_3N_4$ flakes interact with light and the nature of the electronic excitations involved.

Emission spectra from various excited states were examined to understand the material's relaxation pathways. This examination helped clarify the processes through which the material returns to its ground state after excitation.

Assignments of excited states were made by correlating the absorption and emission spectra, allowing for the identification of the electronic states contributing to these processes. This correlation provided a detailed understanding of the energy levels involved in light absorption and emission.

Band structure analysis was performed to determine the positions of the electronic bands, offering insights into the material's redox potentials. This analysis is crucial for understanding the electronic behaviour and potential applications of $g-C_3N_4$.

Finally, the investigation compared the properties of single-layer versus multi-layer $g-C_3N_4$ flakes to assess the effects of dimensionality on the material's optical and electronic characteristics. This comparison helped in understanding how the number of layers influences the overall properties of $g-C_3N_4$.

9.2.3. Theoretical Calculations of Quinoline and 1,10-Phenanthroline Derivatives

Collaborator: Dr Jacek Nycz (University of Silesia, Katowice, Poland)

This project used Gaussian software to calculate the infrared and ultraviolet spectra of quinoline and 1,10-phenanthroline derivative samples. These calculations provided insights into the chromophores' electronic structure and vibrational properties. Additionally, specific molecular orbitals were analysed to better understand the excited-state behaviour of these compounds, which are known for their excited-state intramolecular proton transfer (ESIPT) properties.

9.3. REFERENCES

¹ Apparatus in the Chemistry department of the University of Sheffield (UV-Vis)

² Lord Porter Laser Lab at the University of Sheffield (Helois)

³ GaussView, Version 6.1, Roy Dennington, Todd A. Keith, and John M. Millam, Semichem Inc., Shawnee Mission, KS, 2016.

⁴ Soler, J. M., Artacho, E., Gale, J. D., García, A., Junquera, J., Ordejón, P., & Sánchez-Portal, D. (2002). The SIESTA method for*ab initio*order-Nmaterials simulation. *Journal of Physics: Condensed Matter*, *14*(11), 2745–2779. https://doi.org/10.1088/0953-8984/14/11/302

10. Appendix

CONTENTS

List of Figures	271
List of Tables	272
10.1. Chapter 1	273
10.1.1. Signals in the Soil (SitS) Project Update and Future Plans	273
10.1.1.1. SitS Project Update (Up to October 2023)	273
Soil Analysis at Konza Prairie	273
Soil Organic Matter (SOM) Influence	273
10.1.1.2. SitS Project Future Plans	273
Signal Amplification	273
Interference Ion Testing	273
Real Sample Phosphate Detection	273
Continuous Monitoring Protocol	273
Bluetooth Sensor Integration	273
Field Phosphate Measurement	274
10.2. Chapter 2	275
10.2.1. The Lord Porter Laser Lab and TA System	275
10.3. Chapter 4	276
10.3.1. TA Data Analysis	276
Single-point kinetic fitting function	276
10.3.2. Sample Set 1	277
10.3.2.1. Raman Spectra	277
10.3.2.2. UV- Vis spectra	277
10.3.2.3. Transient Absorption (TA) Pump and Probe	278
Chirp Correction	278
Pump, 400 nm (0.2 µJ) (2.5 KHz)	279
10.3.3. Sample Set 2	
10.3.3.1. Samples Printed on Kapton Tape	
10.3.3.2. Pump-Probe Spectroscopy	
Reflection Mode TA	
Transition Mode TA	
10.3.3.3. XPS results	
10.3.4. Sample Set 3	
10.3.4.1. TEM Images	
10.3.4.2. Estimated Band Gaps via Tauc Plots	
10.3.5. Sample Set 4	

10.3.5.1. Combined Kinetics	287
10.4. Chapter 5	288
10.4.1. Theoretical Calculation Input File	288
Input File Breakdown	289
10.4.2. Initial Testing of Optical Absorption Calculations	292
10.4.3. Other Structures that Were Considered for This Thesis	293
10.5. Chapter 9	294
10.6. References	295

LIST OF FIGURES

Figure 10.1.The Lord Porter Laser Lab (A) The Laser Room, (B) Fs-Transient Absorption Spectrometer

Figure 10.2. TA Sample Interaction Region, Sample: Graphene Film Printed on Quartz Substrate.

Figure 10.3. Raman Spectra of Exfoliated Graphene and Aerosol Gel Graphene Powders

Figure 10.4. Comparing of Normalized UV-Vis Absorption Spectra of Graphene and Aerosol Gel Films

Figure 10.5. Quartz Chirp Curve

Figure 10.6. 400 nm Pump Profile.

Figure 10.7. G III Original Fitted Data and Repeated Data Compared to Power Dependent Data

Figure 10.8. Image of a Select Few AG samples Printed on Kapton Tape

Figure 10.9. TA in Reflection Mode

Figure 10.10. Transient absorption results for AG 0.4 Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 35 to 670 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.6 to 400 ps (left) and its kinetic analysis at different wavelength (right)

Figure 10.11. Transient absorption results for AG 0.5 Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 35 to 670 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.6 to 400 ps (left) and its kinetic analysis at different wavelength (right) and its kinetic analysis at different wavelength (right)

Figure 10.12. XPS of all the sample set two, Five Printed Passes AG samples printed on quartz

Figure 10.13. TEM Images of AG Samples

Figure 10.14. Kinetics Traces at 550 nm for Sample Set 3 and Sample Set 4, Normalised to the Maximum Signal, Highlighting the Recovery Dynamics of the Negative $\Delta T/T$ Signal.

Figure 10.15. An Example of an fdf File part 1

Figure 10.16. An Example of an fdf File part 2

Figure 10.17. Calculated Optical Spectra of Graphene with All Band Considered Compared to Graphene with 26 Bands Considered.

Figure 10.18. Calculated Optical Spectra of a Single Layer of Graphene Compared to Two Layers and Three Layers.

Figure 10.19. Graphene with 20% Curvature in the Zigzag Direction with Various Oxygen Functionalities: (left) epoxide, (middle) substitutional oxygen, (right) a pair of hydroxyls.

Figure 10.20. Graphene with 20% Curvature in the Armchair Direction with Various Oxygen Functionalities: (left) epoxide and (right) substitutional oxygen

Figure 10.21. Calculated Band Structures of Single-Walled CNTs

Figure 10.22. Calculated Optical Properties of Oxygen Functionalised Single-Walled Armchair CNT Compared to Pristine 5n5m Armchair CNT (left), DOS of Oxygen Functionalised Single Walled Armchair CNT Compared to Pristine 5n5m Armchair CNT (right).

LIST OF TABLES

Table 10.1 Pump Parameters for One of the TA Experiments of G I, G II and G III Samples
Table 2 Table Identifying all of the G and AG Printed on Kapton Tape Samples
Table 10.3 Early Time Kinetics of AG 0.4 on Kapton (45-750 fs)
Table 10.4 Late Time Kinetics of AG 0. on Kapton (0.7 ps - 400 ps)
Table 10.5 Early Time Kinetics of AG 0.5 on Kapton (45-750 fs)
Table 10.6 Late Time Kinetics of AG 0.5 on Kapton (0.7 ps - 400 ps)

Appendix

10.1. CHAPTER 1

10.1.1. Signals in the Soil (SitS) Project Update and Future Plans

10.1.1.1. SitS Project Update (Up to October 2023)

This phase of the Signals in the Soil (SITS) project has focused on fabricating printed graphene electrochemical sensors through additive manufacturing technology. These sensors utilise high-quality graphene ink and have been employed to selectively identify phosphate $(H_2PO_4^-)$ ions using an electrochemical detection method.

Soil Analysis at Konza Prairie

The soils studied from the Konza Prairie site were identified as sandy loam, characterised by their calcareous nature with elevated concentrations of calcium and magnesium. Apatite $(Ca_3(PO_4)_2)$ has been identified as a potential primary source of PO_4^{3-} ions in these soils.

Soil Organic Matter (SOM) Influence

The soils contain humic-like, terrestrially derived, relatively decomposed, and aromatic soil organic matter. This SOM likely plays a significant role in mobilising phosphate ions by obstructing their adsorption on aluminium (AI) and iron (Fe) oxide surfaces, thereby enhancing the bioavailability of phosphates in the soil.

10.1.1.2. SitS Project Future Plans

The SitS project will focus on several critical areas of development and testing to further advance the utility and application of the printed graphene electrochemical sensors:

Signal Amplification

The next steps will involve efforts to enhance the sensitivity of the graphene sensors through signal amplification techniques. This will allow for more accurate detection of phosphate concentrations, even at lower levels.

Interference Ion Testing

Future experiments will evaluate the effect of interference from other ions present in the soil matrix, ensuring that the sensors are selective and reliable under varying soil conditions.

Real Sample Phosphate Detection

The project will extend the application of graphene sensors to real soil samples beyond controlled lab environments. This will involve measuring phosphate concentrations in natural and agricultural soils.

Continuous Monitoring Protocol

A key objective will be to develop a simplified, user-friendly protocol for continuous monitoring of phosphate levels in the soil. This protocol will use fully printed graphene electrodes and aim for ease of use in field conditions.

Bluetooth Sensor Integration

Efforts will be made to integrate the graphene sensors with Bluetooth communication modules. This integration will facilitate wireless data transmission, enabling real-time monitoring and remote data collection.

Field Phosphate Measurement

Field measurements are planned as part of the ongoing research. This phase will involve collecting soil samples from various field sites and applying the graphene sensors to assess phosphate levels in situ.

10.2. CHAPTER 2

10.2.1. The Lord Porter Laser Lab and TA System



(a) Laser room 10 KHz Ti: Sapphire laser – 800 nm 40 fs FWHM



(b) TA room 440 – 700 nm probe and 400 nm pump 2500 spectra per second acquired

Figure 10.1.The Lord Porter Laser Lab (A) The Laser Room, (B) Fs-Transient Absorption Spectrometer ¹



Figure 10.2. TA Sample Interaction Region, Sample: Graphene Film Printed on Quartz Substrate.

10.3. CHAPTER 4

10.3.1. TA Data Analysis

Single-point kinetic fitting function²

A single exponential function convolved with a Gaussian function (i(t)) Was used, or if required, a sum of the convoluted functions we used. The function resulting from the convolution is shown below.

$$S(t; A, k, t_0, \widehat{\Delta}) = exp(-kt) \exp\left(k\left(t_0 + \frac{k\widehat{\Delta}^2}{2}\right)\right) \left(1 + \operatorname{erf}\frac{\left(t - (t_0 + k\widehat{\Delta}^2)\right)}{\sqrt{2}\widehat{\Delta}}\right) A$$
(10.1)

The full width at half maximum (FWHM) of the Gaussian function, Δ , is related to $\widehat{\Delta}$ by,

$$\Delta = 2\widehat{\Delta}\sqrt{\ln\left(2\right)} \tag{10.2}$$

The lifetime, τ , is related to the rate, k, by,

$$\tau = \frac{1}{k} \tag{10.3}$$

The position of the maximum of the Gaussian function is given by t_0 .

The Gaussian function, modelling the Instrument Response Function (IRF), is given below.

$$i(t) = \frac{1}{\widehat{\Delta}\sqrt{2\pi}} exp\left(-\ln\left(2\right)\left(\frac{2(t-t_0)}{\Delta}\right)^2\right)$$
(10.4)

10.3.2. Sample Set 1

10.3.2.1. Raman Spectra



Figure 10.3. Raman Spectra of Exfoliated Graphene and Aerosol Gel Graphene Powders³

10.3.2.2. UV- Vis spectra



Figure 10.4. Comparing of Normalized UV-Vis Absorption Spectra of Graphene and Aerosol Gel Films

10.3.2.3. Transient Absorption (TA) Pump and Probe

Chirp Correction

In ultrafast transient absorption spectroscopy, ensuring temporal alignment between the pump and probe pulses is essential for precise measurement of spectral dynamics. The presence of group velocity dispersion (GVD) in the probe pulse results in varied temporal delays for different wavelengths, causing a time-dependent shift in the recorded signal. This temporal dispersion, typically on the order of picoseconds, necessitates meticulous consideration to reliably derive kinetic and spectral insights from the transient absorption data.⁴

Figure 10.5 illustrates the chirp correction applied to the raw transient absorption data. The observed curvature in the pre-analysed data indicates the chirp curve, where shorter wavelengths arrive earlier than longer wavelengths due to the GVD of the probe pulse in the medium (quartz, in this case). The solid line labelled " t_0 fit" represents the temporal correction applied to align the signals across the spectral range.

Equation (10.5) describes the chirp-induced temporal dispersion

$$\Delta T = d \times GVD_{\lambda_1} \times (\lambda_2 - \lambda_1)^5 \tag{10.5}$$

Where ΔT is the time delay, d is the propagation distance, and λ_1 and λ_2 are the wavelengths of interest. Correcting for this dispersion is essential to avoid distortions in the extracted spectra and ensure an accurate interpretation of the excited-state dynamics.

In this case, the temporal dispersion of approximately 1 picosecond (ps) across the spectral range highlights the importance of applying chirp correction, particularly for short-lived excited states where even small timing errors can lead to significant inaccuracies in the measured dynamics. Therefore, by applying the chirp correction, the spectral data can be more accurately aligned in time, enabling precise characterisation of the transient species and their kinetics.



Figure 10.5. Quartz Chirp Curve



Pump, 400 nm (0.2 μJ) (2.5 KHz)

Figure 10.6. 400 nm Pump Profile.
Fable 10.1 Pump Parameters	for One of the	TA Experiments of	f G I, G II and	G III Samples
----------------------------	----------------	-------------------	-----------------	---------------

absorption at an excitation wavelength	energy per excitation pulse / µJ	number of photons per excitation pulse	fraction of photons absorbed	excited state density / cm ⁻²
0.3	0.36	7.24411E+11	3.61346E+11	1.80673E+15



G III

Figure 10.7. G III Original Fitted Data and Repeated Data Compared to Power Dependent Data

10.3.3. Sample Set 2

10.3.3.1. Samples Printed on Kapton Tape Table 2 Table Identifying all of the G and AG Printed on Kapton Tape Samples

Sample name	Oxygen content in the precursor	Treatment	printer passes
1 graphene diluted annealed	n/a	annealed	1
2 graphene diluted annealed	n/a	annealed	2
3 graphene diluted annealed	n/a	annealed	3
1 0.3 diluted annealed	0.3	annealed	1
2 0.3 diluted annealed	0.3	annealed	2
3 0.3 diluted annealed	0.3	annealed	3
1 0.3 annealed	0.3	annealed	1
2 0.3 annealed	0.3	annealed	2
3 0.3 annealed	0.3	annealed	3
1 0.4 annealed	0.4	annealed	1
2 0.4 annealed	0.4	annealed	2
3 0.4 annealed	0.4	annealed	3
1 0.5 annealed	0.5	annealed	1
2 0.5 annealed	0.5	annealed	2
3 0.5 annealed	0.5	annealed	3
1 0.75 annealed	0.75	annealed	1
2 0.75 annealed	0.75	annealed	2
3 0.75 annealed	0.75	annealed	3
1 0.3 annealed	0.3	annealed	1
2 0.3 annealed	0.3	annealed	3
3 0.3 annealed	0.3	annealed	5
1 0.4 annealed	0.4	annealed	1
2 0.4 annealed	0.4	annealed	3
3 0.4 annealed	0.4	annealed	5
1 0.5 annealed	0.5	annealed	1
2 0.5 annealed	0.5	annealed	3
3 0.5 annealed	0.5	annealed	5
1 0.75 annealed	0.75	annealed	1
2 0.75 annealed	0.75	annealed	3
3 0.75 annealed	0.75	annealed	5
1 0.3 unannealed	0.3	unannealed	1
2 0.3 unannealed	0.3	unannealed	3
3 0.3 unannealed	0.3	unannealed	5
1 0.4 unannealed	0.4	unannealed	1
2 0.4 unannealed	0.4	unannealed	3
3 0.4 unannealed	0.4	unannealed	5
1 0.5 unannealed	0.5	unannealed	1
2 0.5 unannealed	0.5	unannealed	3
3 0.5 unannealed	0.5	unannealed	5
1 0.75 unannealed	0.75	unannealed	1
2 0.75 unannealed	0.75	unannealed	3
3 0.75 unannealed	0.75	unannealed	5



Figure 10.8. Image of a Select Few AG samples Printed on Kapton Tape

10.3.3.2. Pump-Probe Spectroscopy *Reflection Mode TA*



Figure 10.9. TA in Reflection Mode

Transition Mode TA



Figure 10.10. Transient absorption results for AG 0.4 Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 35 to 670 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.6 to 400 ps (left) and its kinetic analysis at different wavelength (right).

AG 0.4 on Kapton early time lifetimes							
Wavelength (nm)	Wavelength (nm) $\tau 1$ (fs) $\pm \tau 1$ error $\tau 2$ (fs)						
450	88.4	2.0	~	0.0			
500	95.5	2.0	~	0.0			
550	111.6	1.7	~	0.0			
600	123.7	2.8	~	0.0			
650	120.1	3.2	~	0.0			

Table 10.3 Early	Time Kinetics of	AG 0.4 on Kapton	(45-750 fs)
------------------	------------------	------------------	-------------

Table 10.4 Late Time Kinetics of AG 0. on Kapton (0.7 ps - 400 ps)

AG 0.4 on Kapton late time lifetimes								
Wavelength (nm)	τ1 (ps)	± T1 error	τ2 (ps)	± T2 error	τ3 (ps)	± T3 error	τ4 (ps)	±т4 error
450	0.092	0.002	5.130	91.436	5.423	115.939	∞	0.000
500	0.115	0.001	3.690	78.445	3.803	114.544	∞	0.000
550	0.119	0.003	3.033	62.773	2.832	48.102	∞	0.000
600	0.115	0.003	1.271	0.317	∞	0.000	n/a	
650	0.113	0.001	3.279	8.935	4.153	13.354	∞	0.000



Figure 10.11. Transient absorption results for AG 0.5 Printed on Kapton Tape After 400 nm Excitation (1.0 mW). Top graphs show the transient change in transmission in a short time window of 35 to 670 fs (left) and its kinetic analysis at different wavelength (right), bottom graphs show the transient change in transmission in a longer time window of 0.6 to 400 ps (left) and its kinetic analysis at different wavelength (right).

AG 0.5 on Kapton early time lifetimes						
Wavelength (nm)	± T2 error					
450	88.6	3.4	~	0.0		
500	100.1	1.8	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.0		
550	113.6	2.0	~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~~	0.0		
600	125.8	2.2	~	0.0		
650	129.8	3.3	8	0.0		

Table 10.5 Early Time Kinetics of AG 0.5 on Kapton (45-750 fs)

Table 10.6 Late Time Kinetics of AG 0.5 on Kapton (0.7 ps - 400 ps)

AG 0.5 on Kapton late time lifetimes								
Wavelength (nm)	τ1 (ps)	± T1 error	τ2 (ps)	± T2 error	τ3 (ps)	± T3 error	τ4 (ps)	± т4 error
450	0.094	0.006	41.525	12.045	∞	0.000	n/a	
500	0.100	0.001	61.926	8.506	~	0.000	n/a	
550	0.113	0.002	0.473	0.093	55.264	6.025	0.000	n/a
600	1.094	0.264	0.124	0.002	42.900	7.468	n/a	
650	0.123	0.003	0.763	0.242	85.287	27.229	~	0.000

10.3.3.3. XPS results



Figure 10.12. XPS of all the sample set two, Five Printed Passes AG samples printed on quartz

10.3.4. Sample Set 3

10.3.4.1. TEM Images



(a) AG 0.4



(b) AG 0.75

Figure 10.13. TEM Images of AG Samples

10.3.4.2. Estimated Band Gaps via Tauc Plots

Tauc plots are a graphical method used to estimate the optical bandgap of semiconductors. The optical bandgap represents the minimum energy (eV) required to excite an electron from the valence band to the conduction band using light. UV-Vis spectroscopy is used to measure the absorption coefficient

(α) of the material at different wavelengths of light. The absorption coefficient indicates how strongly the material absorbs light at a specific wavelength. A Tauc plot shows the square root of the product of the absorption coefficient (α) and the photon energy ($h\nu$) on the y-axis versus the photon energy ($h\nu$) on the x-axis. Here, h is Planck's constant and ν is the frequency of light. The plot often exhibits a linear region at higher photon energies. Extrapolating this linear region to the x-axis (where the y-axis value becomes zero) gives the estimated value of the optical bandgap.

The appropriate Tauc plot model for graphene and graphene oxide depends on the specific electronic band structure and the material's properties. In a direct bandgap material, efficient light absorption can directly excite an electron from the valence band to the conduction band. In an indirect bandgap material, light absorption might involve the simultaneous emission or absorption of a phonon to conserve momentum during the electron transition.

Ideal single-layer graphene has a zero bandgap due to its remarkable honeycomb lattice structure. This means electrons can move freely between valence and conduction bands without an energy barrier. When oxygen functional groups, such as epoxides and hydroxyls, are introduced to graphene, it disrupts its perfect structure and may create a bandgap. The exact nature of the bandgap, whether it is direct or indirect, can depend on the specific type and concentration of oxygen functionalities present. This is further studied theoretically in Chapter 5. Some studies suggest that graphene oxide (GO or rGO) with lower oxygen content might exhibit a direct bandgap. As the oxygen content increases, the bandgap might become indirect.⁶

Using a method described in a research paper in 2018,⁷ the Tauc plots of the AG on quartz samples were calculated. The data was collected in the form of percentage reflectance against wavelength (%R vs nm). The Tauc method is based on the assumption that the energy-dependent absorption coefficient α can be related to the photon frequency and the band gap by equation (10.6).

$$(\alpha . hv)^{1/\gamma} = A (hv - E_a)$$
(10.6)

Where α is the absorption coefficient (units of cm⁻¹), h is Planck's constant (6.626 x 10⁻³⁴ J s), ν is the frequency of light (Hz), γ is the exponent related to the nature of the electronic transitions (e.g., 2 for direct bandgap materials), A is for a related to the material's properties and E_g is the bandgap energy (eV).

For Tauc plots the above formula is written as the Kubelka- Munk Equation, as shown in Equation (10.7).⁸

$$[F(R_{\infty})hv]^{\gamma} = A (hv - E_g)$$
(10.7)

Where $F(R_{\infty})$ is the Kubelka-Munk function, defined as:

$$F(R_{\infty}) = \frac{k}{s} = \frac{(1 - R_{\infty})^2}{2R_{\infty}}$$
(10.8)

Here, k is the absorption coefficient (units of m⁻¹) and s is the scattering coefficient (units of m⁻¹ R_{∞} refers to the reflectance at an infinitely thick sample.

To simplify for practical purposes, the function of reflectance is typically written as:

$$F(R) = \frac{(1-R)^2}{2R}$$
(10.9)

where **R** is the reflectance measured during the experiment.

The energy hv, with units of eV, can be calculated using:

$$hv = Energy = \frac{1240}{\lambda(nm)} \tag{10.10}$$

Two separate plots were generated for each sample using these equations to analyse the bandgap properties of the AG samples. Equation 10.11, used for direct bandgap transitions, is:

 $[F(R)hv]^{1/2} = A(hv - E_g)$, units of (eV cm⁻¹)^{1/2} And for indirect bandgap transitions, Equation (10.12) is applied: (10.11)

$$[F(R)hv]^2 = A(hv - E_g), \text{ units of } (eV \text{ cm}^{-1})^2$$
(10.12)

10.3.5. Sample Set 4

10.3.5.1. Combined Kinetics



Figure 10.14. Kinetics Traces at 550 nm for Sample Set 3 and Sample Set 4, Normalised to the Maximum Signal, Highlighting the Recovery Dynamics of the Negative $\Delta T/T$ Signal.

10.4. CHAPTER 5

10.4.1. Theoretical Calculation Input File

1	SolutionMethod diagon		
T	SystemLabel A4by4Graphene		
	# MD options		
	MD.TypeOfRun	CG	# Type of dynamics:
	MD.NumCGsteps	500	# Number of CG steps for
			# coordinate optimization
2	MD MaxCGDispl	0 1 Ang	# Maximum atomic displacement
2	monnaxeeospi	# in c	ne CG step (Bohr)
	MD MayForceTol	0.01 oV/Apg	# Tolerance in the maximum
	MD.MaxForceToi	0.01 eV/Ang	# rolerance in the maximum
			# atomic force (Ky/Bohr)
	MD.VariableCell	false	
	#MD.VariableCell	true	#Optimise lattice parameters
	OpticalCalculation true		
	Optical.EnergyMinimum 0.0 Ry		
	Optical.EnergyMaximum 2 Ry		
3	Optical.Broaden 0.2 eV		
	#Optical.NumberOfBands 26		
	%block Optical.Mesh		
	24 24 1		
	%endblock OpticalMesh		
	~		
	# Basis		
	%block PAO Basis		
	C 2		
	0-202540.00		
	n=2 0 2 E 40-0.9		
	5.94869034392 2.5090419		
	n=2 1 2 E 40 -0.9		
4	7.63838693570 2.6226139		
	n=2 2 1 E 40 -0.9 Q 6.4005365 .	0100000	
	7.63838693570		
	%endblock PAO.Basis		
	#PAO.Energyshift	5 meV	
	#PAo.BasisSize	DZP	
	##KgridCutoff	118.056 Ang	# Corresponds to a 96 96 96 mesh
		S	
	#KgridCutoff	0.0 Ang	
-	%block kgrid Monkhorst Pack		
5	24 0 0 0		
	0 24 0 0		
	0010		
	%endblock kgrid Monkhorst P	ack	
	%endblock kgrid_Monkhorst_P	ack	
	<pre>%endblock kgrid_Monkhorst_P</pre>	ack	
	%endblock kgrid_Monkhorst_P	VDW	# Evolution of the strength of
6	%endblock kgrid_Monkhorst_P	VDW	# Exchange-correlation functional
6	%endblock kgrid_Monkhorst_P	VDW LMKLL	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P xc.functional xc.authors MeshCutoff 250.0	VDW LMKLL Ry	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0	VDW LMKLL Ry	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho	VDW LMKLL Ry .true.	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P xc.functional xc.authors MeshCutoff 250.0 #SaveRho	VDW LMKLL Ry .true.	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential	VDW LMKLL Ry .true. .true.	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential	VDW LMKLL Ry .true. .true.	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options	VDW LMKLL Ry .true. .true.	# Exchange-correlation functional # Exchange-correlation version
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MaxSCFIterations	VDW LMKLL Ry .true. .true.	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options [MaxSCFIterations [DM.MixingWeight]	VDW LMKLL Ry .true. .true. 1000 0.0125	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveRho #SaveElectrostaticPotential [# SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle
6 7	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance	vDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0] #SaveRho #SaveElectrostaticPotential [# SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential [# SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDM	Ack VDW LMKLL Ry .true. .true. .true. 1000 0.0125 0.0125 1.d-4 false false	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential [# SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDAta DM.NumberPulav	vDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false false 5	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential #SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDAta DM.NumberPulay SolutionMethod diagon	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false false 5	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors [MeshCutoff 250.0] #SaveRho #SaveElectrostaticPotential #SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDAta DM.NumberPulay SolutionMethod diagon	VDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false false 5	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDM UseSaveDAta DM.NumberPulay SolutionMethod diagon ##ElectronicTemperature	Ack VDW LMKLL Ry .true. .true. .true. 1000 0.0125 0.0125 1.d-4 false false false 5	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MAXSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveDM UseSaveData DM.NumberPulay SolutionMethod diagon ##ElectronicTemperature	vDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false 5 25 meV	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files # Temp. for Fermi smearing
6 7 8	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential # SCF options MAXSCFIterations DM.MixingWeight DM.Tolerance DM.UseSaveDM UseSaveDM UseSaveDAta DM.NumberPulay SolutionMethod diagon ##ElectronicTemperature # Output options	vDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false false 5 25 meV	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files # Temp. for Fermi smearing
6 7 8 9	%endblock kgrid_Monkhorst_P [xc.functional xc.authors MeshCutoff 250.0 #SaveRho #SaveElectrostaticPotential #SCF options MaxSCFIterations DM.MixingWeight DM.KickMixingWeight DM.Tolerance DM.UseSaveDM UseSaveData DM.NumberPulay SolutionMethod diagon ##ElectronicTemperature # Output options LongOutput	vDW LMKLL Ry .true. .true. 1000 0.0125 0.0125 1.d-4 false false 5 25 meV true	# Exchange-correlation functional # Exchange-correlation version # Maximum number of SCF iter # New DM amount for next SCF cycle # Tolerance in maximum difference # between input and output DM # to use continuation files # Temp. for Fermi smearing

Figure 10.15. An Example of an fdf File part 1

```
WriteMullikenPop
                                    1
      WriteCoorXmol true
9
      WriteMDXmol true
       WriteCoorStep true
      NumberOfSpecies
                                    1
32
      NumberOfAtoms
      %block ChemicalSpeciesLabel
      1 6 C
%endblock ChemicalSpeciesLabel
      LatticeConstant
                                    1.00000 Ang
10
      SaveElectrostaticPotential
                                    .true.
       %block LatticeVectors
                                                                0.00000000000000E+000
       9.838
                                    0.00000000000000E+000
       0.000000000000000E+000
0.00000000000000E+000
                                    8.52000033855438
                                                                0.00000000000000E+000
                                    0.00000000000000E+000
                                                                30.00
       %endblock LatticeVectors
       AtomicCoordinatesFormat Ang
      %block AtomicCoordinatesAndAtomicSpecies
```

	0.000000000000	0.000000000000	0.0000000000	000	1# C	1
	0.000000000000	1.420000000000	0.000000000	000	1# C	2
	1.229750000000	2.130000000000	0.0000000000	000	1# C	3
	1.229750000000	3.550000000000	0.000000000	000	1# C	4
	2.459500000000	4.260000000000	0.0000000000	000	1# C	5
	2.459500000000	5.68000000000	0.000000000	000	1# C	6
	3.689250000000	6.390000000000	0.000000000	000	1# C	7
	8.608250000000	-0.71000000000	0.000000000	000	1# C	8
	2.459500000000	0.000000000000	0.0000000000	000	1# C	9
	2.459500000000	1.420000000000	0.0000000000	000	1# C	10
	3.689250000000	2.130000000000	0.0000000000	000	1# C	11
	3.689250000000	3.550000000000	0.0000000000	000	1# C	12
	4.919000000000	4.260000000000	0.0000000000	000	1# C	13
	4.919000000000	5.680000000000	0.000000000	000	1# C	14
	6.148750000000	6.390000000000	0.0000000000	000	1# C	15
11	1.229750000000	-0.71000000000	0.000000000	000	1# C	16
50	4.919000000000	0.000000000000	0.0000000000	000	1# C	17
	4.919000000000	1.420000000000	0.0000000000	000	1# C	18
	6.148750000000	2.130000000000	0.0000000000	000	1# C	19
	6.148750000000	3.550000000000	0.0000000000	000	1# C	20
	7.378500000000	4.260000000000	0.0000000000	000	1# C	21
	7.378500000000	5.68000000000	0.0000000000	000	1# C	22
	8.608250000000	6.39000000000	0.0000000000	000	1# C	23
	3.689250000000	-0.71000000000	0.000000000	000	1# C	24
	7.37850000000	0.000000000000	0.000000000	000	1# C	25
	7.378500000000	1.420000000000	0.0000000000	000	1# C	26
	8.608250000000	2.130000000000	0.0000000000	000	1# C	27
	8.608250000000	3.550000000000	0.000000000	000	1# C	28
	0.000000000000	4.260000000000	0.0000000000	000	1# C	29
	0.00000000000	5.680000000000	0.000000000	000	1# C	30
	1.229750000000	6.390000000000	0.000000000	000	1# C	31
	6.148750000000	-0.71000000000	0.000000000	000	1# C	32
	(%endblock Atomic	CoordinatesAndA	tomicSpecies			
	WFS.Write.For.Bar	nds .true.				
	BandLinesScale Re	ciprocalLatticeVec	tors			
	%block BandLines					
	1 0.0000000000	0.000000000 0	.0000000000	\GA	AMMA	
12	40 0.333333333	0.000000000 0	.0000000000	Ρ		
	40 0.500000000	0.0000000000	0.0000000000	х		
	40 0.500000000	0.5000000000	0.0000000000	S		
	40 0.000000000	0.500000000	0.0000000000	Y		
	40 0.0000000000	0.0000000000	0.00000000000	\G/	AMMA	
	%endblock BandLin	nes				
	%block ProjectedD	ensityOfStates				
13	-10.00 0 0.05 50	00 eV				
	-					

%endblock ProjectedDensityOfStates

Figure 10.16. An Example of an fdf File part 2

Input File Breakdown

1. Header Information

SolutionMethod diagon: Specifies the method used to solve the Schrödinger equation, in this case, diagonalisation.

SystemLabel A4by4Graphene: Sets the label for the simulated system, which in this case is a 4x4 graphene lattice.

2. Atom Dynamics Options

MD.TypeOfRun CG: The type of dynamics used is conjugate gradient (CG), which optimises the system's geometry.

MD.NumCGsteps 500: Sets the maximum number of Conjugate Gradient steps to 500.

MD.MaxCGDispl 0.1 Ang: Limits the maximum displacement of atoms per step to 0.1 Ångström.

MD.MaxForceTol 0.01 eV/Ang: Specifies the convergence criterion, where the maximum force tolerance is 0.01 eV/Å.

MD.VariableCell false: Disables optimization of lattice parameters, keeping the cell fixed.

3. Optical Properties Calculation

OpticalCalculation true: Enables the calculation of optical properties.

Optical.EnergyMinimum 0.0 Ry and Optical.EnergyMaximum 2 Ry: Defines the energy range for the optical calculations, from 0 to 2 Rydberg.

Optical.Broaden 0.2 eV: Sets the broadening parameter for optical spectra to 0.2 eV.

%block Optical.Mesh...%endblock OpticalMesh: Defines a 24x24x1 mesh for sampling the Brillouin zone during optical calculations.

4. Atomic Basis Set

%block PAO.Basis...%endblock PAO.Basis: Specifies the basis set for carbon atoms, including orbital information, energy cutoffs, and other parameters essential for electronic structure calculations.

5. K-Point Sampling

%block kgrid_Monkhorst_Pack...%endblock kgrid_Monkhorst_Pack: Defines a Monkhorst-Pack grid for k-point sampling, specifically a 24x24x1 grid for integrating over the Brillouin zone.

6. Exchange-Correlation Functional

xc.functional VDW and xc.authors LMKLL: Specifies the exchange-correlation functional to be used, in this case, a van der Waals (VDW) functional according to the LMKLL authors.⁹⁻¹⁰

7. Mesh Cutoff

MeshCutoff 250.0 Ry: Sets the mesh cutoff for real-space integration to 250 Rydberg, which affects the precision of the calculation.

8. Self-Consistent Field (SCF) Options

MaxSCFIterations 1000: Limits the maximum number of SCF iterations to 1000.

DM.MixingWeight 0.0125 and DM.KickMixingWeight 0.0125: Specifies the mixing weights for density matrix updates during the SCF cycle.

DM.Tolerance 1.d-4: Sets the convergence tolerance for the density matrix, with a value of 1e-4.

DM.UseSaveDM false and UseSaveData false: Disables the use of saved density matrix and data from previous calculations.

DM.NumberPulay 5: Defines the number of Pulay mixing steps for the SCF procedure.

9. Output Options

LongOutput true: Enables detailed output information.

WriteMullikenPop 1: Requests the Mulliken population analysis to be written to the output.

WriteCoorXmol, WriteMDXmol, and WriteCoorStep true: Enables output of atomic coordinates in XMOL format and for each MD step.

10. System Definition

NumberOfSpecies 1 and NumberOfAtoms 32: Defines the system as having 1 species (carbon) and 32 atoms.

%block ChemicalSpeciesLabel...%endblock ChemicalSpeciesLabel: Labels species, where '1' corresponds to carbon (atomic number 6).

LatticeConstant 1.00000 Ang: Sets the lattice constant, used for scaling the lattice vectors.

%block LatticeVectors...%endblock LatticeVectors: Defines the lattice vectors for the simulation cell, including the lengths and directions.

11. Atomic Coordinates

AtomicCoordinatesFormat Ang: Specifies that atomic coordinates are provided in Ångström units.

%block AtomicCoordinatesAndAtomicSpecies...%endblock AtomicCoordinatesAndAtomicSpecies: Lists the atomic coordinates and species, where each line gives the x, y, and z coordinates and the species label (in this case, all carbon atoms).

12. Band Structure Calculation

WFS.Write.For.Bands .true.: Enables writing the wavefunctions for band structure calculations.

BandLinesScale ReciprocalLatticeVectors: Indicates that band lines are scaled using reciprocal lattice vectors.

%block BandLines...%endblock BandLines: Specifies the path in the Brillouin zone for the band structure calculation, including points like Γ, P, X, S, and Y.

13. Projected Density of States (PDOS) Calculation

%block ProjectedDensityOfStates...%endblock ProjectedDensityOfStates: This block sets up the calculation for the projected density of states (PDOS). The parameters inside the block define the energy range and resolution for the PDOS calculation:

- -10.00: Sets the lower energy limit to -10 eV.
- 0: Sets the upper energy limit to 0 eV.
- 0.05: Specifies the peak width, set to 0.05 eV.
- 500: Indicates the number of sampling points in the energy range.
- eV: Specifies that the energy units are in electron volts (eV).

10.4.2. Initial Testing of Optical Absorption Calculations



Figure 10.17. Calculated Optical Spectra of Graphene with All Band Considered Compared to Graphene with 26 Bands Considered.



Figure 10.18. Calculated Optical Spectra of a Single Layer of Graphene Compared to Two Layers and Three Layers.

10.4.3. Other Structures that Were Considered for This Thesis



Figure 10.19. Graphene with 20% Curvature in the Zigzag Direction with Various Oxygen Functionalities: (left) epoxide, (middle) substitutional oxygen, (right) a pair of hydroxyls.



Figure 10.20. Graphene with 20% Curvature in the Armchair Direction with Various Oxygen Functionalities: (left) epoxide and (right) substitutional oxygen

10.5. CHAPTER 9



Figure 10.21. Calculated Band Structures of Single-Walled CNTs



Figure 10.22. Calculated Optical Properties of Oxygen Functionalised Single-Walled Armchair CNT Compared to Pristine 5n5m Armchair CNT (left), DOS of Oxygen Functionalised Single Walled Armchair CNT Compared to Pristine 5n5m Armchair CNT (right).

10.6. REFERENCES

¹ Department of Chemistry, University of Sheffield, Lord Porter Laser Laboratory

² Auty, A. J., Negar Mansouriboroujeni, Nagaraja, T., Dimitri Chekulaev, Sorensen, C. M., Das, S. R., Martsinovich, N., & Adrien. (2022). Ultrafast Transient Absorption Spectroscopy of Inkjet-Printed Graphene and Aerosol Gel Graphene Films: Effect of Oxygen and Morphology on Carrier Relaxation Dynamics. *The Journal of Physical Chemistry C*, *126*(18), 7949–7955. https://doi.org/10.1021/acs.jpcc.2c01086

³ Department of Physics, Kansas State University

⁴ Megerle, U., Pugliesi, I., Schriever, C., Sailer, C. F., & Riedle, E. (2009). Sub-50 fs broadband absorption spectroscopy with tunable excitation: putting the analysis of ultrafast molecular dynamics on solid ground. *Applied Physics B*, *96*(2-3), 215–231. <u>https://doi.org/10.1007/s00340-009-3610-0</u>

⁵ Bor, Zs., & Rácz, B. (1985). Group velocity dispersion in prisms and its application to pulse compression and travelling-wave excitation. *Optics Communications*, *54*(3), 165–170. <u>https://doi.org/10.1016/0030-4018(85)90284-6</u>

⁶ Bagri, A., Mattevi, C., Acik, M., Chabal, Y. J., Chhowalla, M., & Shenoy, V. B. (2010). Structural evolution during the reduction of chemically derived graphene oxide. *Nature Chemistry*, *2*(7), 581–587. <u>https://doi.org/10.1038/nchem.686</u>

⁷ Makuła, P., Pacia, M., & Macyk, W. (2018). How To Correctly Determine the Band Gap Energy of Modified Semiconductor Photocatalysts Based on UV–Vis Spectra. *The Journal of Physical Chemistry Letters*, *9*(23), 6814–6817. <u>https://doi.org/10.1021/acs.jpclett.8b02892</u>

⁸ Kubelka, P., & Munk, F. (1931). *An Article on Optics of Paint Layers*. <u>http://www.graphics.cornell.edu/~westin/pubs/kubelka.pdf</u>

⁹ Lee, K., Murray, É. D., Kong, L., Lundqvist, B. I., & Langreth, D. C. (2010). Higher-accuracy van der Waals density functional. *Physical Review B*, *82*(8). <u>https://doi.org/10.1103/physrevb.82.081101</u>

¹⁰ Artacho, E., María, J., Barcelona, C., Center, S., Gale, J., García, A., Junquera, J., Martin, R., Papior, N., & Soler, J. (2021). <u>https://siesta-project.org/SIESTA_MATERIAL/Docs/Manuals/siesta-4.1.5.pdf</u>