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Structuring and Functionalisation of Chemical Vapour Deposited Graphene

A thesis presented to the University of Dublin, Trinity College

for the degree of

Doctor of Philosophy in Chemistry

by

Sinéad Winters

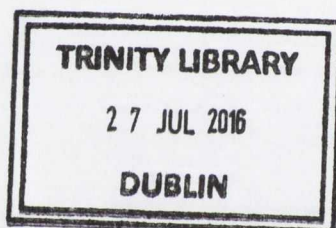


Under the supervision of Prof. Georg S. Duesberg

School of Chemistry & CRANN

Trinity College Dublin

2016



Thesis 10932

Declaration

I declare that this thesis has not been submitted as an exercise for a degree at this or any other university and it is entirely my own work. Due acknowledgement and references are given to the work of others where appropriate.

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Sinéad Winters, September 2015



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Abstract

Graphene has fascinated researchers since its discovery in 2004 due to its extraordinary physical, electrical and optical properties. In order to exploit its potential for industrial applications, the mass production of graphene must be optimised. One of the most promising methods for large-scale synthesis is chemical vapour deposition (CVD), which produces high-quality graphene films on a metallic substrate. For most applications, the graphene must subsequently be transferred from the metal to its target substrate using a polymer-assisted transfer process.

This thesis presents the structuring and non-covalent functionalisation of CVD graphene through the modification of the polymer-assisted transfer process. The introduction of folds and wrinkles into a graphene sheet alters its chemical and electronic properties, and its surface chemistry can be altered by the introduction of functional groups through covalent or non-covalent functionalisation. This tailoring of graphene's physical and chemical properties is important for applications in electronics and sensors.

The first section of this thesis describes 3D structures of graphene produced by integrating a printing step into the transfer process. The 3D graphene is supported by a polymer scaffold. The conformation of graphene to the scaffold was characterised using atomic force and scanning electron microscopy. The structures were investigated through Raman spectroscopy

to ascertain the presence of strain and doping in the graphene. Electrochemical measurements indicate that the surface area of the structured samples has been increased due to the folding of the graphene over the scaffold.

The remainder of the thesis discusses the non-covalent functionalisation of graphene with a perylene derivative. The packing density of the molecules on the graphene is investigated using Raman spectroscopy, water contact angle and scanning tunnelling microscopy. The presence of contamination from the polymer transfer process influences the packing density of the molecules on the graphene surface, with higher density films being produced by deposition onto graphene that has been annealed to reduce residue. In order to remove the need for the time-consuming annealing step, an alternative transfer process, termed functional layer transfer (FLaT), was developed. In this process, the molecules are deposited on the as-grown graphene on copper and subsequently transferred along with the graphene to the target substrate. After transfer, the molecules are present in a highly-packed, stable layer similar to that produced by deposition onto annealed graphene.

The efficiency of FLAT was demonstrated by comparing the performance of functionalised graphene field effect transistors. Transistors manufactured with the FLAT method demonstrated superior gas sensing performance compared to devices functionalised after graphene transfer. In addition, the higher packed molecule films produced by FLAT showed increased stability during an on-surface derivatisation process.

In summary, the alteration of graphene by the modification of the transfer process as been achieved using two methods. The integration of a transfer printing step has resulted in the production of folded graphene structures. The development of FLAT provides a streamlined method for producing non-covalently functionalised graphene.

Publication Highlights

Certain work presented within this thesis has been published in peer-reviewed journals. This section serves to highlight these papers.

Some of the work presented in Chapter 4 features in the following paper:

1. "Production of 3D-shaped graphene *via* transfer printing"

Sinéad Winters, Toby Hallam, Hugo Nolan, Georg S. Duesberg, *physica status solidi b*, **249** (12), 2515-2518 (2012)

Chapters 5 and 7 feature elements from the following papers:

1. "Understanding and optimising the packing density of perylene bisimide layers on CVD-grown graphene"

Nina C. Berner, **Sinéad Winters**, Claudia Backes, Chanyoung Yim, Kim C. Dömbgen, Izabela Kaminska, Sebastian Mackowski, Attilio A. Cafolla, Andreas Hirsch, Georg S. Duesberg, *Nanoscale*, **7**, 16337-16342 (2015)

2. "On-surface derivatisation of aromatic molecules on graphene: The importance of packing density"

Sinéad Winters, Nina C. Berner, Rohit Mishra, Kim C. Dömbgen, Claudia Backes, Martin Hegner, Andreas Hirsch, Georg S. Duesberg, *Chemical Communications*, **51**, 16778-16781 (2015)

Abbreviations

- 1: Perylene derivative 1
- 2D: 2-dimensional
- 3D: 3-dimensional
- AFM: Atomic force microscopy
- APS: Ammonium persulfate
- CAB: Cellulose acetate butyrate
- CV: Cyclic voltammetry
- CVD: Chemical vapour deposition
- *E. coli*: *Escherichia coli*
- EDA: Ethylenediamine
- EDC: 1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride
- FLaT: Functional layer transfer
- FWHM: Full width half maximum
- GFET: Graphene field effect transistor

- HATU: O-(7-Azabenzotriazole-1-yl)-N,N,N,N-tetramethyluronium hexafluorophosphate
- NHS: *N*-hydroxysuccinimide
- OTS: Octadecyltrichlorosilane
- PDMS: Poly(dimethylsiloxane)
- PMMA: Poly(methylmethacrylate)
- PEI: Poly(ethylene imine)
- PTCDA: Perylene-3,4,9,10-tetracarboxylic dianhydride
- SAM: Self-assembled monolayer
- SEM: Scanning electron microscopy
- STM: Scanning tunnelling microscopy
- sulfo-NHS: *N*-hydroxysulfosuccinimide
- UV: Ultraviolet
- vis: Visible
- WCA: Water contact angle
- XPS: X-ray photoelectron spectroscopy

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Chapter 1

Introduction

1.1 Graphene

Graphene has fascinated researchers since it was first experimentally produced in 2004. Initially believed to be unstable and therefore only useful for theoretical studies,¹ the discovery of isolated graphene flakes led to a flurry of investigation into the material's properties and potential applications.^{2,3} Over a decade later, graphene still maintains its reputation as one of the most fascinating nanomaterials and attracts a large level of investment from science funding institutes and private companies.⁴

Graphene is a single layer of sp^2 -hybridised carbon atoms arranged in a honeycomb structure, as depicted in Figure 1.1. It was first experimentally produced in 2004 by Novoselov *et al.* through the exfoliation of a single layer from a crystal of graphite using a piece of sticky tape.⁵ This isolation of single-layer graphene sheets allowed the properties of graphene to be experimentally investigated for the first time. For this reason, Konstantin Novoselov and Andre Geim received the Nobel prize in physics in 2010.⁶ Graphene has several properties that have led to its popularity: it exhibits extremely high

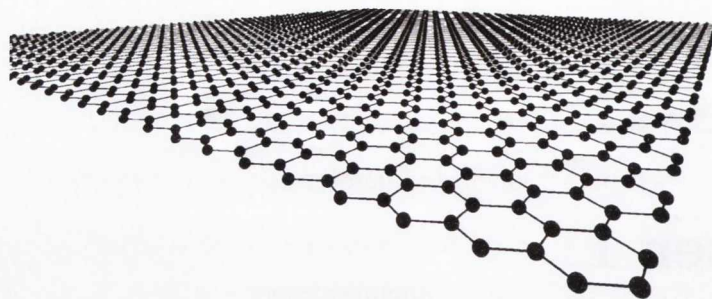


Figure 1.1: Illustration of atomic structure of graphene.

charge carrier mobilities (up to $200,000 \text{ cm}^2/\text{V}\cdot\text{s}$) at room temperature,⁷ and an exceptional Young's modulus of 1 TPa.⁸ In addition, a graphene monolayer transmits approximately 97% of incident light,⁹ rendering it useful for transparent electrodes such as touch screens and solar cells.^{10–12} Due to its two-dimensional (2D) nature, graphene is extremely sensitive to its external environment. The sensitivity can be exploited for sensor applications and has led to the investigation of graphene as a transducer for chemical and biological sensors.^{13–15}

Large-scale and reliable production and processing of graphene is required in order to meet its potential for all applications.³ The original method of mechanical exfoliation is insufficient for production of graphene on an industrial scale. Therefore methods of large-scale production, such as chemical vapour deposition (CVD), have been developed since its discovery. CVD of graphene produces continuous, large-area graphene films on a metallic substrate.^{16,17} The subsequent transfer of CVD graphene from the metal to an insulating substrate is an area of intense research as optimisation of this process will allow for very clean, large-area graphene films that can be integrated into device architectures.^{18,19} Depending upon the application, this integration is usually achieved by post-transfer processing, such as additional lithogra-

phy steps or functionalisation. The main focus of this thesis is integrating the structuring and functionalisation with the transfer process in order to avoid additional fabrication steps and therefore reduce contamination of the graphene surface.

1.2 Scope of Thesis

This thesis is centred on the modification of the standard transfer process of CVD graphene in order to produce folded three-dimensional (3D) structures or to functionalise a graphene surface. A brief literature review of each relevant research area is given at the beginning of chapters 4-7 in order to provide context to the results produced and the conclusions drawn.

This chapter gives a brief outline of graphene and the properties that have led to such wide interest in the material. The second chapter contains more detailed background theory on graphene production methods and the experimental methods used in this thesis. The third chapter gives details on the experimental equipment used to produce the results presented in the subsequent chapters.

Chapter 4 details the production of 3D-shaped graphene through the use of patterned stamps of polydimethylsiloxane (PDMS). The conformation of the graphene on the stamps and the final printed structures is characterised using scanning electron microscopy (SEM) and atomic force microscopy (AFM). The effects of strain and doping due to contact with polymers is assessed through Raman spectroscopic analysis. It is concluded that strain is released while the graphene is on the PDMS stamps and therefore the shifts in the Raman peak positions are due to doping from the polymer substrate. The increase in surface area due to the folding of the graphene is

demonstrated through electrochemical measurements.

In chapter 5, the functionalisation of graphene with an aromatic molecule is described. The effect of polymer residues on the packing density of the molecules is ascertained using Raman spectroscopy. An alternative method of producing functionalised graphene, termed functional layer transfer (FLaT), is introduced. This method produces functionalised graphene by deposition of the molecules prior to polymer-assisted transfer. The orientation of the molecules on the graphene surface is determined using scanning tunnelling microscopy (STM) and fluorescence measurements. It is observed that the molecules adsorb perpendicular to the graphene surface, which is contrary to other studies which have demonstrated a planar conformation for molecules containing a large aromatic core.

Chapter 6 details the fabrication of functionalised graphene field effect transistors produced by FLAT and by post-transfer molecule deposition. The characteristics of the devices indicate that the molecules n-dope graphene. The devices produced by FLAT exhibit higher electron mobility than post-transfer functionalised devices, indicating that the denser layer of molecules passivates the surface of the graphene. This is further evidenced in the assessment of the transistors as gas sensors for ammonia and nitrogen dioxide. Functionalised devices exhibit a stable response with higher signal-to-noise than that of bare graphene. The FLAT produced devices demonstrate the lowest limit of detection for both gasses.

Chapter 7 describes the on-surface derivatisation of the functional groups of the molecules from carboxylic acid to amine groups. It is found that the molecular packing density on the graphene surface is incredibly important for the stability of the molecules during the reaction process. The subsequent amine-derivatised films are characterised using Raman and X-ray photoelec-

tron spectroscopy (XPS). The ability of the amine functionalised films to attract bacteria to the graphene surface is demonstrated using fluorescence microscopy.

Chapter 8 concludes the thesis and discusses future work that could be undertaken using the techniques developed within this document.

Chapter 2

Background Theory

2.1 Large-Scale Graphene Synthesis

Graphene was first produced by exfoliating single layers from a crystal of graphite using a piece of tape.⁵ Although the scotch tape method developed by Novoselov *et al.* produces the most pristine monolayer graphene with superior electronic and mechanical properties, the process suffers from low throughput and is only capable of producing small areas of isolated graphene flakes. In an effort to produce graphene on a larger scale, several methods have been developed which will be discussed in the following sections.

2.1.1 Liquid-Phase Exfoliation

Liquid-phase exfoliation produces dispersions of graphene flakes by application of ultrasonic energy or shear forces that separate bulk graphite into small flakes of material.^{20,21} Initially, this method involved the use of potentially carcinogenic organic solvents²⁰ but a method involving the use of surfactants in aqueous solutions to separate the graphene flakes has been developed.²² These flakes can subsequently be drop-cast or sprayed onto a

substrate to form a film of graphene. Although this method produces large amounts of flakes at relatively low cost, it is difficult to control flake size and the number of layers formed during the deposition process. Therefore, graphene flakes or films fabricated by this method are not suitable for high-performance electronics. However, they still have potential applications in energy storage^{23,24} and also in composite materials as an additive to increase mechanical strength.²⁵

Liquid-phase exfoliation can also be employed using graphite oxide, a layered material consisting of graphite sheets with oxygen functionalities on the basal plane and edges.²⁶ Due to the presence of oxygen moieties, graphite oxide is easily exfoliated in aqueous solution to produce stable dispersions.²⁷ A monolayer of this material is referred to as graphene oxide, which can subsequently be reduced to graphene through the use of thermal²⁸ or chemical²⁷ means. However, the reduction process can lead to a high amount of structural defects within the flakes, resulting in reduced mechanical and electrical performance. Therefore, materials formed by this process are typically referred to as reduced graphene oxide, to reflect their different properties to pristine graphene. The functionalisation of the basal plane is useful in some applications, such as electrochemical electrodes, due to the presence of reactive functional groups.²⁹

2.1.2 Sublimation of Si from Silicon Carbide

Epitaxial growth of graphene on silicon carbide is achieved by heating the SiC substrate to approximately 1100 °C in order to sublime the silicon atoms from the surface, leaving layers of graphene behind.³⁰ The graphene formed by this method consists of crystals reaching tens of microns in size. While the top layer of graphene is generally unaffected by the SiC substrate underneath,

deeper layers are subject to significant amounts of strain due to the lattice mismatch between graphene and the SiC surface.³¹ Epitaxial graphene is generally used in UHV studies as it can be created on the SiC substrate and subsequently examined without breaking vacuum, therefore ensuring that the substrate remains free of contamination. These studies usually focus on the electrical properties of the graphene on the substrate^{30,32} or self-assembly of molecules on the graphene surface.³³ Molecular self assembly on epitaxial graphene will be discussed further in Chapter 5.

2.1.3 Chemical Vapour Deposition

Chemical vapour deposition (CVD) is a technique that produces films of material by the decomposition of precursors onto a substrate. In the case of graphene, a transition metal substrate is required to catalyse the reaction. Typical metals for graphene growth include nickel and copper and the most common precursor is methane. CVD growth on nickel results in multiple layers of graphene due to the high solubility of carbon at the growth temperature. Upon cooling, the carbon layers segregate to the surface resulting in a film that consists of multiple layers of graphitic carbon.³⁴ The solubility of carbon in copper is much lower at the growth temperature; therefore this process tends to yield mostly monolayer graphene films.¹⁶ The presence of hydrogen is necessary to catalyse the growth but the ratio of hydrogen to methane must be carefully controlled as high partial pressures of hydrogen etch the edges of graphene flakes formed on the substrate.³⁵

Once the graphene has been synthesised on a metal film, typically it must then be transferred to the target substrate for the desired application. A typical transfer process consists of spinning a polymer, typically polymethylmethacrylate (PMMA), over the graphene on the metal substrate,

etching of the metal and then fishing the graphene onto the desired target substrate (SiO_2 , glass, etc).³⁶ The PMMA is then removed using acetone. This process is the most widely used transfer process for CVD graphene, however it does suffer from the presence of polymer residues which can degrade electronic device performance.³⁷ Several methods of removing the polymer residue have been explored, including vacuum annealing,³⁷ and different methods of PMMA removal in acetone.³⁸ Recently, the use of cellulose-based polymers in place of PMMA has been proposed, which produces cleaner films with better electrical properties.³⁹ Through the use of these various techniques the production of clean, large-area graphene films is now possible. CVD graphene films tend to suffer from lower mobility than flakes produced using the mechanical exfoliation method due to grain boundaries,⁴⁰ however mobilities close to that of exfoliated graphene have recently been achieved.⁴¹ These studies validate the potential of CVD for production of high-quality, high-mobility graphene which could be used for high-performance electronics, sensors, touch screens and solar-cell electrodes. The quality of graphene obtained by the various production methods is summarised in Figure 2.1. From this graph it can be seen that CVD graphene is currently the most viable option for achieving performance similar to that produced by mechanical exfoliation, especially when the cost of mass production is taken into account.³

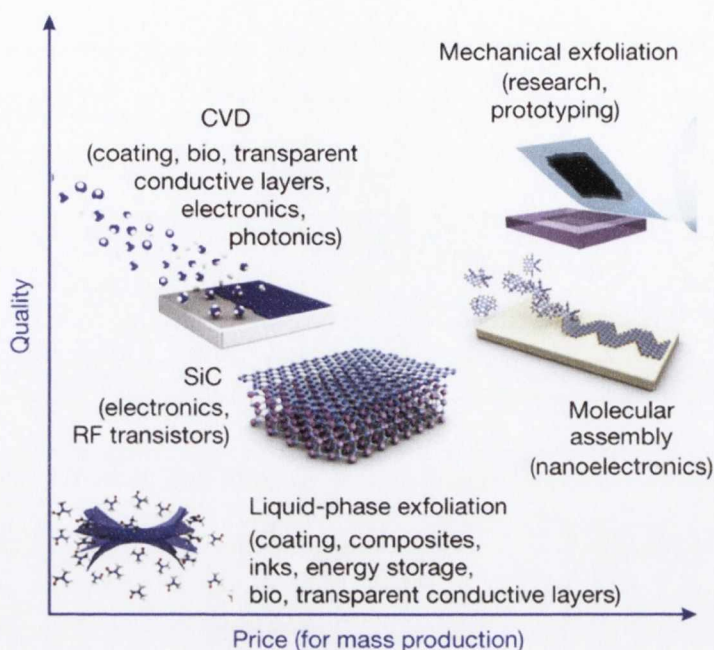


Figure 2.1: Methods of graphene production compared by quality of graphene produced versus cost for mass production. Potential applications of the various graphene qualities are also listed. Image obtained from Novoselov *et al.*³

2.2 Characterisation Techniques

2.2.1 Raman Spectroscopy

Raman spectroscopy is a spectroscopic method that uses the inelastic scattering of monochromatic light to investigate the vibrational modes of a sample.⁴² It was first observed by C.V. Raman and K.S. Krishnanin in 1928,⁴³ for which Raman received the Nobel prize in physics in 1930. Typically, when a photon strikes a material, it undergoes elastic (Rayleigh) scattering with no change in energy. However, some photons (approximately 1 in 10^7) are scattered inelastically, causing a small shift in their energy. These small

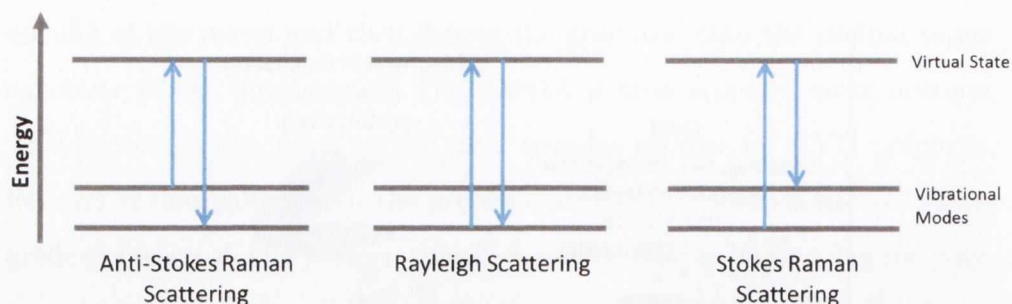


Figure 2.2: Schematic of the types of scattering that occur upon illumination of a material by light.

shifts are detected in Raman spectroscopy. During the inelastic scattering, the photon excites an electron to a virtual energy state. Upon relaxation, the electron returns to a state of slightly higher or lower energy, emitting a photon corresponding to this energy change. These shifts are referred to as Stokes and anti-Stokes shifts, respectively, and are depicted in Figure 2.2. Typically, the Stokes signals are more intense than the anti-Stokes as at room temperature the majority of molecules are in the ground state.

The intensity of the Raman signal, I_R is given by:

$$I_R = \nu^4 I_0 N \left(\frac{\partial \alpha}{\partial Q} \right)^2 \quad (2.1)$$

where ν is the frequency of the excitation light, I_0 is the incident intensity, N is the number of scattering molecules, α is the polarisability of the molecules and Q is the vibrational amplitude. If the excitation energy is close to that of an electronic transition within a material, the intensity is greatly increased. This process is called resonant Raman scattering. From equation 2.1, it can be seen that a change in polarisability of the molecule must occur in order for a Raman signal to be observed. This is a fundamental selection rule and differentiates Raman spectroscopy from infra-red (IR) spectroscopy, where a

change in dipole moment of a molecule is required. Materials that produce Raman peaks are said to be Raman active. Each material has a unique spectrum, which is useful in identifying and characterising substances present in a sample.

Raman Spectrum of Graphene

There are three main peaks in the graphene spectrum: the D ($\sim 1350\text{ cm}^{-1}$), G ($\sim 1580\text{ cm}^{-1}$) and 2D ($\sim 2700\text{ cm}^{-1}$) peaks. The G peak is typical of sp^2 -hybridised carbons, as it corresponds to their in-plane vibrations.⁴⁴ The D peak is associated with a breathing mode of the aromatic ring and is only present in defective graphene samples. It is indicative of defects in the graphene lattice due to broken bonds, grain boundaries or lattice vacancies.⁴⁵ This peak does not appear in the spectrum of a graphene sample with a pristine crystal lattice. When present, the ratio of the intensities of the D and G bands (I_D/I_G) can indicate crystallite size and the continuity of a graphene film.⁴⁶

The D band is a single-phonon process, while the 2D band is the two-phonon overtone. The 2D band stems from a double resonance process involving two phonons at the zone boundary.^{45,47} The scattering events leading to the D and 2D band are depicted in Figure 2.3. An incident photon causes an electron to be excited to a state marked by a . The electron is scattered from here to another electronic state, b , by elastic interaction with a defect (D band) or an inelastic interaction with a phonon (2D band). The electron is then scattered by a phonon interaction to position c , from where it recombines with a hole to relax back to d by emission of a photon. These processes are called intervalley processes as the electron is scattered from the K to K' positions of the graphene Brillouin zone.

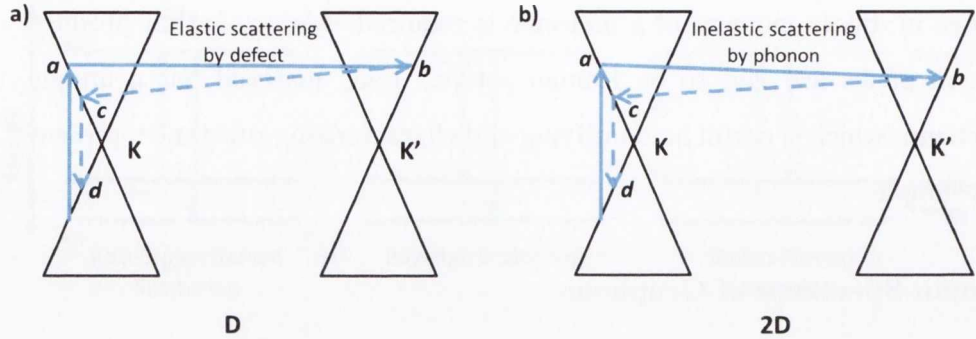


Figure 2.3: a) Scattering mechanism for graphene D band. The electron is excited to a at the K position by the incident light. If a defect is present, the electron is scattered to b in the K' position. It is then inelastically scattered to position c by a phonon interaction and returns to d by emitting a photon. b) Scattering mechanism for graphene 2D band. The electron is excited to a at the K position by the incoming light, then inelastically scattered by a phonon to b in the K' position. Another inelastic scattering event by a phonon brings the electron to position c , where it returns to d by photon emission.

The Raman spectra of graphene and graphite are depicted in Figure 2.4a and are taken in the centre of highly ordered sheets, therefore the D peak is not visible. The 2D peak is of particular interest as it can be used to differentiate between single and multi-layer graphene.⁴⁵ As seen in Figure 2.4a, the graphene 2D peak is a single sharp peak whose intensity is approximately four times that of the G peak. Monolayer graphene is generally indicated by an intensity ratio of 3-4 between the 2D and G bands (I_{2D}/I_G). The monolayer 2D peak can also be fitted as a sharp Lorentzian peak with a full-width at half-maximum (FWHM) of $\sim 30 \text{ cm}^{-1}$, which broadens as further graphene layers are added and begins to resemble graphite when five graphene layers are present (Figure 2.4b). This is due to interactions between the π and π^* bands as further layers are added. The bands split into four and provide additional contributions to the 2D band.⁴⁵ This feature of graphene's spectrum has increased the importance of Raman spectroscopy as a means

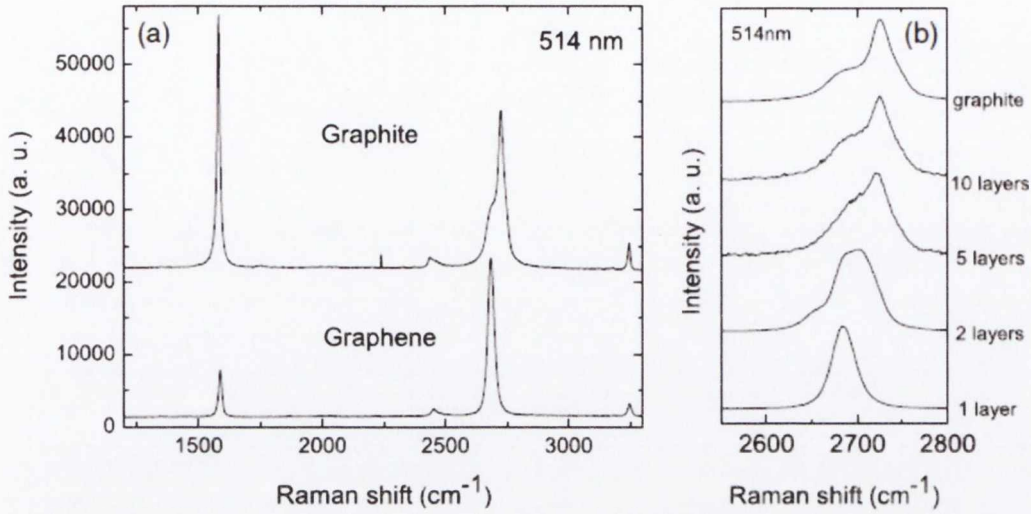


Figure 2.4: a) Raman spectrum of graphite and graphene under 514 nm excitation. b) Evolution of graphene 2D peak with additional layers. This image is adapted from Ferrari *et al.*⁴⁵

of characterising graphene samples. Analysis of the shape, position and relative intensity of the 2D peak presents a simple, fast and non-destructive method of determining the number of layers in a sample in comparison with other methods, such as transmission electron microscopy and atomic force microscopy.

Strain and Doping in Graphene

Raman spectroscopy can also be used to determine the amount of strain or doping within a graphene sample. The position of the G and 2D peaks is influenced by both of these factors. In the case of strain, red-shifting⁴⁸ and splitting of the G peak have been reported.⁴⁹ In unstrained graphene, the vibrations associated with the G mode are symmetric in the x and y directions. When uniaxial strain greater than 0.3% is applied, the symmetry is broken, resulting in two separate peaks, dubbed G^+ (higher band) and

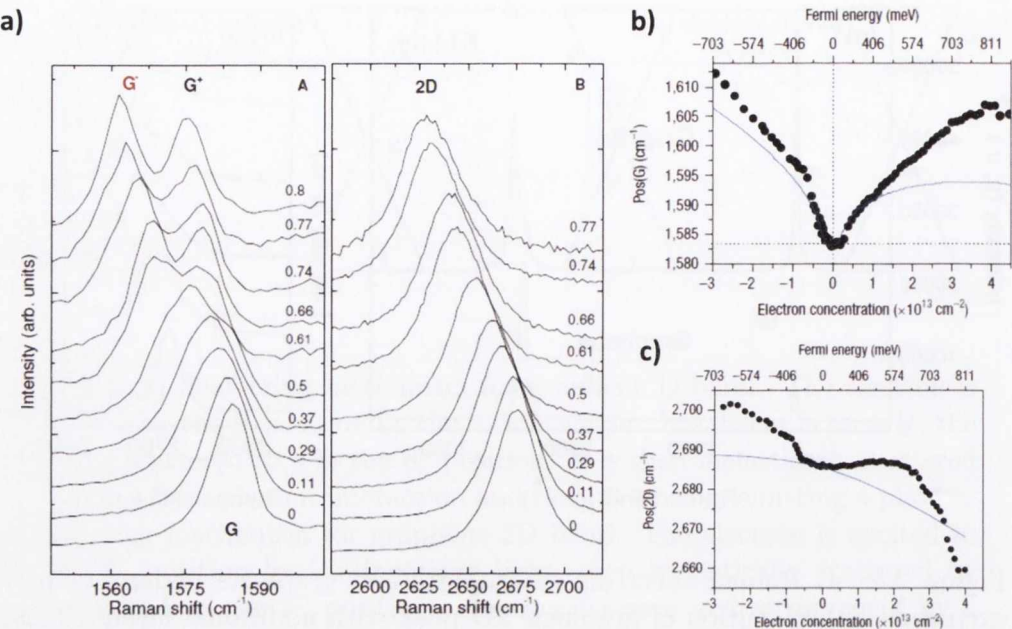


Figure 2.5: a) Splitting of G peak and change in 2D peak position due to uniaxial strain. (b) Change in G and c) 2D peak position due to charge doping. Figure adapted from Mohiuddin *et al.* and Das *et al.*^{49,50}

G⁻ (lower band). The 2D peak is also red-shifted with strain, but no peak-splitting is observed. These shifts are depicted in Figure 2.5a.

Charge doping occurs through transfer of electrons or holes between graphene and its substrate, which raises or lowers the Fermi level of the graphene. The G peak moves to higher wavenumbers (blueshifts)⁵⁰ and narrows⁵¹ from a FWHM of $\sim 15 \text{ cm}^{-1}$ to $\sim 8 \text{ cm}^{-1}$ in response to both electron and hole-doping. The 2D peak position is sensitive to the type of charge carriers injected into graphene, shifting to lower wavenumbers in the case of electron (n-type) doping or higher wavenumbers for hole (p-type) doping.⁵⁰ The variation of the G and 2D peak positions with charge doping is shown in Figure 2.5b and c.

In order to differentiate between strain and charge doping, the FWHM

of the G band and the shifts in the position of the G and 2D bands must be compared.⁵¹ Where the FWHM of G is less than 15 cm^{-1} , doping is present and the direction of the 2D shift indicates the type of doping. Where the FWHM of G is greater than 15 cm^{-1} , the shifts in the 2D and G bands can be attributed to strain. In this case, the ratio of the change in positions of the G and 2D band would be approximately 2.

2.2.2 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is a widely used technique to acquire high-resolution images of samples on the micro- and nanoscale.⁵² A beam of electrons is scanned across the surface of a sample. When the electrons enter the sample, multiple interactions arise such as backscattering of the original electron beam and production of secondary and Auger electrons, as shown in Figure 2.6. Other events such as X-ray emission can also occur.

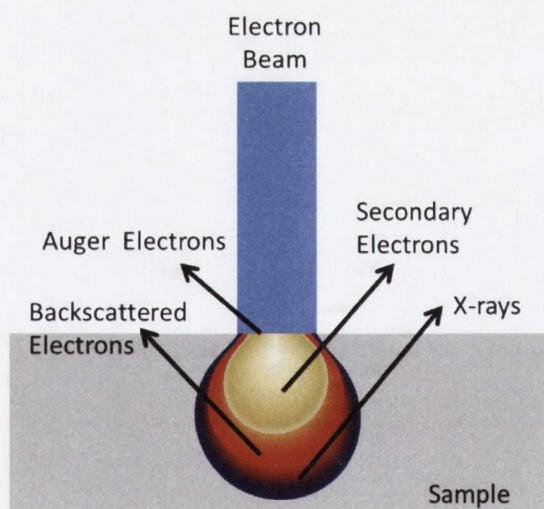


Figure 2.6: Schematic of interactions and events within a sample when interacting with an electron beam.

These interactions create signals that are measured by various detectors and used to create images of the sample. Images created using the secondary electron signal give topographical information, as secondary electrons generally only emanate from the surface or a very small depth within the sample. Backscattered electrons are generated by the scattering of incident electrons in the sample and they provide information on the chemical composition of the sample surface.

2.2.3 Atomic Force Microscopy

Atomic force microscopy (AFM) is a type of scanning probe microscopy consisting of a sharp probe (tip) placed on the end of a cantilever which is rastered across the surface of the sample.⁵³ A laser is reflected off the surface of the cantilever onto a photodetector, as shown in Figure 2.7. The movement of the laser spot on the detector measures minute changes in the position of the cantilever. As the tip scans across the sample, it interacts with

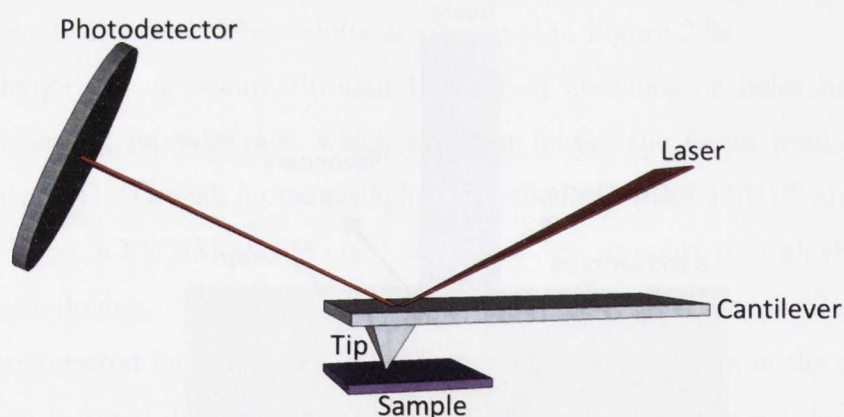


Figure 2.7: Basic diagram of AFM measurement. The AFM cantilever contains a tip near the end which interacts with the sample. Movement of a laser reflected off the back of the cantilever is captured by a photodetector and translated into topographical information of the sample surface.

the surface *via* a variety of forces, such as van der Waals, electromagnetic, and capillary forces, causing the cantilever to deflect. This movement of the cantilever is detected and can be translated into topographic information for the sample surface. The most common mode of operation for AFM is tapping mode. In tapping mode, a voltage is applied to the cantilever causing it to oscillate at a frequency close to its resonant frequency. As the tip is scanned over the surface, van der Waals and other surface forces causes the oscillation of the cantilever to be dampened. The tip-to-sample distance is constantly adjusted via a piezoelectric motor in order to maintain the oscillation of the cantilever at the set value. This constant adjustment translates into an image of the sample surface and provides topographical information on the surface of the sample.

2.2.4 Cyclic Voltammetry

Cyclic voltammetry is an electrochemical technique used to investigate the kinetics of electron transfer on a sample surface.⁵⁴ The cell potential is swept linearly back and forth (cycled) between two setpoints (see Figure 2.8a) and the current at the working electrode is measured. In a typical cyclic voltammogram, peaks are observed corresponding to the oxidation and reduction of the redox couple. In an ideal reversible redox process, the peaks are mirror images of one another. Examination of these peaks can yield information on the kinetics of electron transfer at the electrode and also information on the surface area or the presence of different functional groups in the electrochemically active region.

A typical cyclic voltammogram is shown in Figure 2.8b. The direction of the scan is initially from positive to negative potential, as indicated by the arrow. The peak currents corresponding to anodic and cathodic current

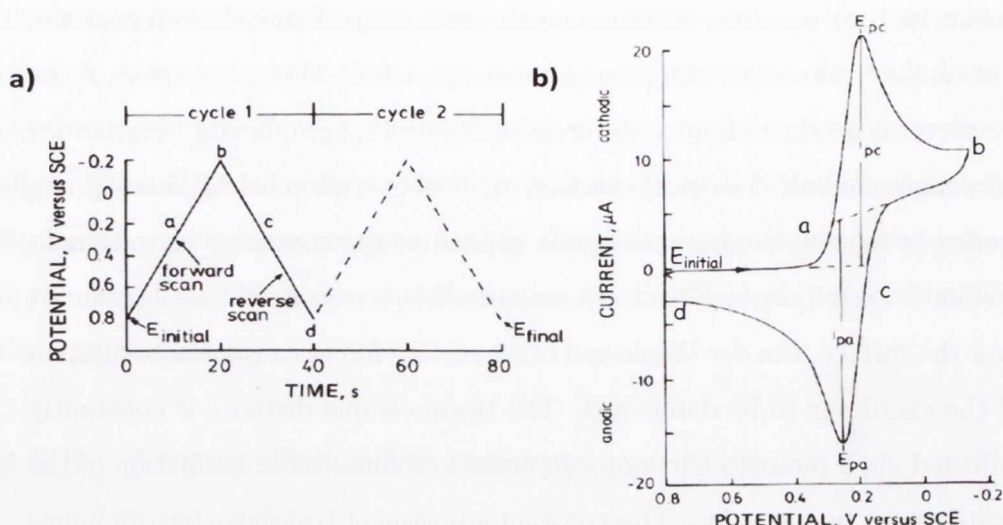


Figure 2.8: a) Potential waveform applied for cyclic voltammetry. b) A typical cyclic voltammogram. Images adapted from Kissinger and Heineman.⁵⁴

(i_{pa} and i_{pc}) and their corresponding potentials (E_{pa} and E_{pc}) are clearly marked. Cathodic and anodic currents correspond to reduction and oxidation processes, respectively. For a reversible process, the cell potential is described using the Nernst Equation shown below, where E is the cell potential, E^0 is the standard cell, R is the universal gas constant, T is temperature, n is the number of electrons transferred in the redox reaction, F is Faraday's constant, and c_O and c_R are the concentrations of the oxidised and reduced species in solution, respectively.

$$E = E^0 + \frac{RT}{nF} \ln \frac{c_O}{c_R} \quad (2.2)$$

As the potential is swept in the negative direction, the concentration of reduced species at the electrode is increased. This leads to a concentration gradient at the electrode which allows current to flow, resulting in the increase in current in the cyclic voltammogram (point a). The current reaches

a maximum (point E_{pc}), and then begins to fall due to the decrease in concentration of the oxidised species at the electrode. The current reaches a stable value that is limited by the diffusion of fresh electrolyte to the electrode. The scan direction is then switched to the positive direction (point b) and the oxidation reaction occurs along the reverse scan.

When a potential is applied to the working electrode, a double layer is formed at the surface of the electrode.⁵⁵ This double layer gives rise to a charging current that can be related to the scan rate by the following equation.

$$I_{dl} = C_{dl}v \quad (2.3)$$

Where C_{dl} is the double layer capacitance and v is the scan rate. The double layer formed at the surface is generally modelled as a parallel plate capacitor, whose capacitance is linearly proportional to its area. Therefore, investigation of the charging current can also yield information on changes to the surface area of an electrode. Charging current is measured with no redox probe present in the system, instead cyclic voltammetry is carried out using solely the background electrolyte.

2.2.5 Water Contact Angle

Water contact angle measurement is a simple technique to identify the presence of polar groups on the surface of a sample. When a water droplet is placed upon a surface, it will form a particular shape depending upon the degree of wettability of the surface. The shape of the droplet can be analysed to determine the contact angle between the water drop and the sample. The contact angle is influenced by the surface tension of the water and the surface tension at the water/solid interface. The tension at the interface is influenced

by the presence of a variety of forces such as van der Waals interactions, polar functional groups and hydrogen bonding. Low contact angles are indicative of a hydrophilic surface, while large contact angles indicate a hydrophobic surface. Typically graphene is considered to be hydrophobic,^{56,57} but the introduction of oxygenated functional groups can lower the contact angle by creation of hydrogen bonds and polar interactions, resulting in a hydrophilic surface.⁵⁶

2.2.6 Fluorescence Techniques

Fluorescence is the emission of light from a material after absorption of electromagnetic radiation.⁵⁸ Upon light absorption, electrons within the material are promoted to higher energy states and emit light upon relaxation. Similar to Raman spectroscopy, a Stokes shift of the emitted light is observed, *i.e.* the light emitted is of a longer wavelength than the absorbed light. This is due to non-radiative energy dissipation within the material prior to light emission, as depicted in Figure 2.9.

Fluorescence spectroscopy provides information on the electronic tran-

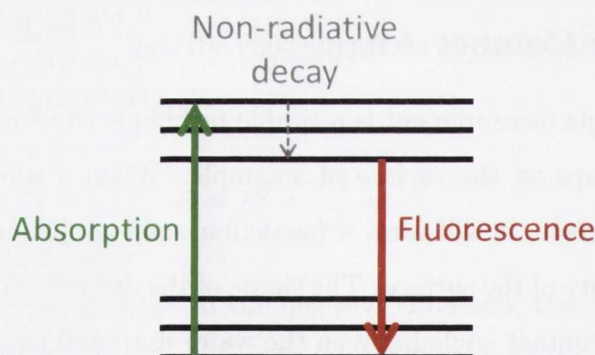


Figure 2.9: Energy diagram of fluorescence emission.

sitions of a sample. After illumination, the light emitted by the sample is measured and recorded as a function of intensity versus wavelength. Changes in intensity can be monitored and quenching of fluorescence can be identified by decreased intensity. Fluorescence quenching occurs when an emitting material (the donor) transfers energy to another material (the acceptor). The efficiency, E , of this energy transfer can be determined using fluorescence lifetime measurements. For these measurements, the fluorophore is excited by a short pulse of light. The intensity of the emitted light is then measured as a function of time. The decay time of the sample can be extracted as the slope from the plot of log of intensity versus time. E is then calculated using the equation:

$$E = 1 - \frac{\tau_{DA}}{\tau_D} \quad (2.4)$$

where τ_{DA} and τ_D denote the fluorescence decay time of the donor in the presence of the acceptor and without the acceptor, respectively.⁵⁹

In addition to studying the properties of a material and its interaction with the environment, fluorescence is also utilised as marker for studying the interactions of cells or non-fluorescent molecules and proteins. This is achieved through the use of fluorescent dyes that are attached to a particular molecule or cell that is to be studied. The position and movements of the cell or molecule can then be imaged using fluorescent microscopy.

2.2.7 Scanning Tunnelling Microscopy

Scanning tunnelling microscopy (STM) is a scanning probe technique that allows the local density of states on the surface of a sample to be imaged down to atomic resolution.⁶⁰ Figure 2.10 demonstrates the basic operating principle behind an STM. A sharp metal tip is brought very close to the surface to be

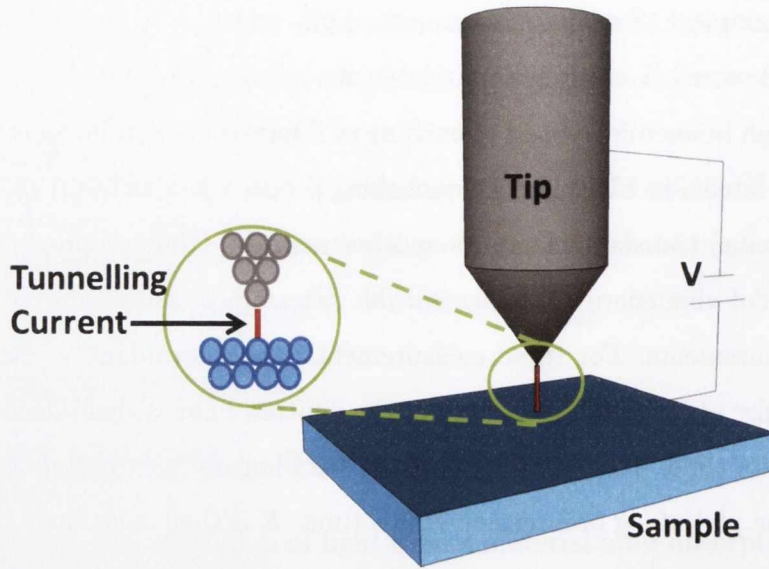


Figure 2.10: Schematic of STM measurement. A metal tip is brought close to the surface of the sample. A bias voltage is applied between the sample and the tip. This leads to a tunnelling current between the topmost atom of the tip and the atoms on the surface.

imaged. A bias voltage, V , applied between the tip and the sample surface allows a small current to flow between the STM probe and the sample, which probes the local density of states of the atoms on the surface. The current is produced due to the quantum mechanical effect of electron tunnelling through an energy barrier. Due to the need for an electrical current to flow, STM is only suitable for studying metallic or semiconducting surfaces.

In classical mechanics, a particle with an energy, E , can only overcome a potential barrier U_0 if $E > U_0$. However, in quantum mechanics the particle is described by the Schrödinger equation:

$$-\frac{\hbar^2}{2m} \frac{\partial^2 \psi(z)}{\partial z^2} + U(z)\psi(z) = E\psi(z) \quad (2.5)$$

When this is solved for $E < U_0$, the solution is the following decaying

wavefunction:

$$\psi(z) = \psi_0 e^{\pm \kappa z} \quad (2.6)$$

where the decay constant, κ , is defined as:

$$\kappa = \frac{\sqrt{2m(U - E)}}{\hbar} \quad (2.7)$$

This results in a non-zero probability of a particle tunnelling through an energy barrier, which is what is exploited in order to obtain STM images.

There are two modes of operation for an STM: (i) constant height mode and (ii) constant current mode. In each mode the tip height or the current are held constant, while the other parameter is measured. The STM is typically operated in constant current mode as the distance between the sample and the tip is controlled *via* a feedback loop, which avoids the tip crashing into the surface.

2.2.8 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy (XPS) is a type of photoemission spectroscopy which utilises the photoelectric effect to analyse the chemical composition of a sample. The photoelectric effect is the emission of electrons from a material upon illumination by light of a sufficient energy. The energy, E_{kin} of the photoelectron is determined by the equation:⁶¹

$$E_{kin} = h\nu - E_B \quad (2.8)$$

$h\nu$ is the energy of the incident photon and E_B is the binding energy of the electron in the material.

Measurement of the kinetic energy of photoelectrons produced by irra-

diating a material with light of a known energy allows the electron binding energy to be calculated. This energy is characteristic of specific elements and therefore can be used to determine the chemical species present within a sample. This is the basic principle behind XPS, which uses X-rays to eject electrons from the core levels of atoms within a sample. The typical output of an XPS measurement is a graph which plots the electron counts against the binding energy, producing peaks that are representative of each element in the sample. High-resolution XPS spectra can also reveal the type of bonding present (e.g. C-C, C-O bonds can be observed in the C 1s XPS peak). The ejected electrons typically originate from the top 1-2 nm of the sample, as electrons originating from deeper atoms will be prevented from escaping the surface due to inelastic collisions with other electrons or atoms. Thus, XPS is a sensitive technique that gives information about the very top surface of the sample, which is useful when characterising very thin materials such as graphene.

Chapter 3

Experimental Methods

3.1 Production Techniques

3.1.1 Materials

All chemicals were purchased from Sigma Aldrich and used as received unless otherwise specified. Polydimethylsiloxane (PDMS) under the brand name Sylgard 184 was purchased from Dow Corning. Aqueous solutions were made using purified water (18 M Ω) from a Barnstead Nanopure Millipore system. SiO₂ substrates were purchased from IDB Technologies and Si-Mat and consisted of dry thermal oxide (150 or 300 nm) on Si(100). Argon (99.99%) and methane (98%) were purchased from BOC Gases. Nitrogen was produced from atmosphere using a DALCO N₂ generator. Hydrogen was produced using a Schmidlin PG-H2 250 H₂ generator. Copper foils (18 μ m) were purchased from GOULD Electronics GmbH.

3.1.2 Chemical Vapour Deposition

Prior to graphene growth the copper foils were immersed in 10% HCl to remove residual oxides. The foils were then rinsed in water and dried with N_2 before being placed in the CVD furnace. The setup for the CVD furnace is shown in Figure 3.1. The furnace was heated to growth temperature with 50 sccm H_2 flow. Graphene was grown *via* chemical vapour deposition for 20 minutes at 1035 °C in a Carbolite quartz tube furnace, with methane as the carbon source. Flow rates for hydrogen and methane were 2.5 sccm and 10 sccm, respectively. The overall pressure in the chamber was approximately 200 mTorr. After growth, the heat source was turned off and the sample was cooled under 2.5 sccm H_2 and 0.5 sccm methane.

3.1.3 Graphene Transfer

For samples of bare graphene on SiO_2 , a standard polymer assisted transfer process for graphene was used as outlined in Section 2.1.3. In this process, graphene grown on copper was sonicated in acetone for 2 mins, followed by rinsing in IPA and dried using N_2 . A polymer was spincoated over the graphene on the copper growth substrate. Typically, PMMA polymer was used; however, in Chapter 6, cellulose acetate butyrate was used as it results in improved electrical performance in comparison with PMMA.³⁹ The copper foil was etched in aqueous ammonium persulfate (APS) solution (1 M).

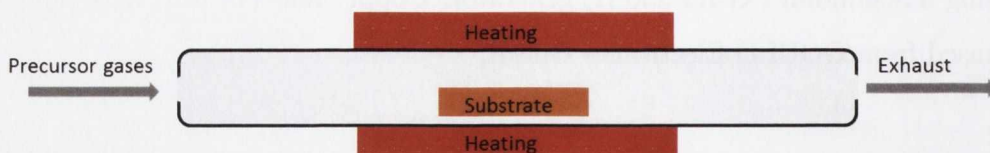


Figure 3.1: Schematic of Carbolite CVD system for graphene growth.

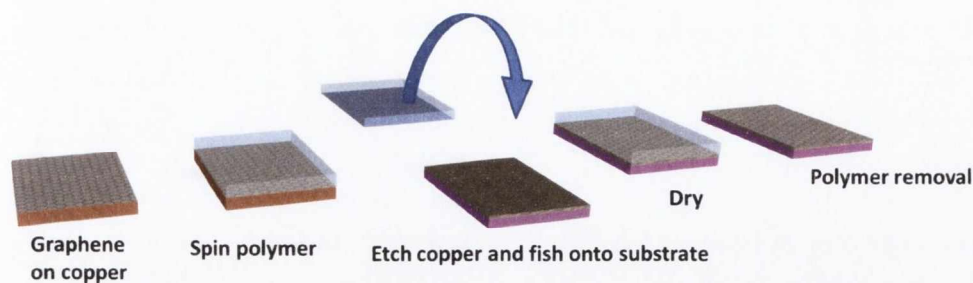


Figure 3.2: Schematic of graphene polymer-assisted transfer process.

The graphene remained adhered to the polymer layer and was transferred to deionised water using a glass slide, where it was subsequently fished onto the target substrate. Upon drying, the polymer was removed by immersion in acetone. The process is outlined in Figure 3.2.

3.1.4 UV Lithography

Ultra-violet (UV) lithography is a well-established method for the micro-patterning of substrates. It is widely used in industrial manufacturing due to its speed and ability to reliably pattern large areas. The UV process for a positive resist is depicted in Figure 3.3. A thin film of photo-sensitive polymer (the resist) is spun onto a substrate and exposed to UV light through a mask

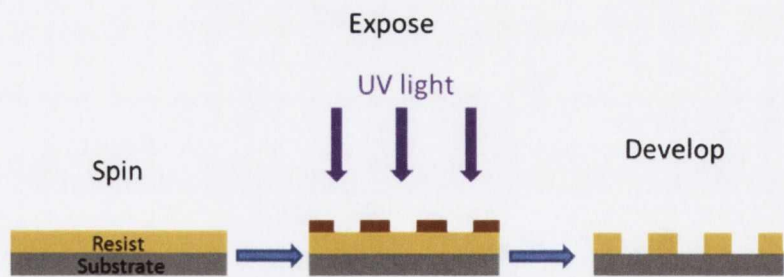


Figure 3.3: UV lithography process consisting of spincoating of the resist, UV exposure and development of the pattern.

containing the desired pattern. For positive resists, the section of polymer exposed to UV becomes more soluble in a solution termed the developer. By placing the substrate into the developer, the exposed polymer is removed. For negative resists, the opposite process occurs and the polymer not exposed to UV is removed.

UV lithography in this thesis was carried out using S1813 resist (a positive resist) and MF 319 developer. UV exposure was carried out using an Optical Associates Incorporated (OAI) Mask Aligner.

3.1.5 Plasma Etching

Plasma is a state of matter in which the molecules or atoms are ionised. Due to its excited state, plasma is incredibly reactive. This property is exploited in plasma etching, where a plasma reactant is accelerated toward a substrate in order to remove material from the surface. Plasma etching is highly anisotropic, therefore it can be used to etch sharp features into a substrate that has been previously patterned using lithography techniques. The process is depicted schematically in Figure 3.4.

Plasma etching was used in this thesis to create trenched silicon moulds. The silicon was patterned with lines using UV lithography, as shown in Fig-

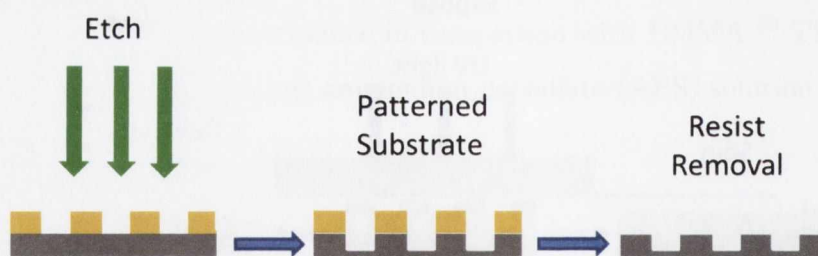


Figure 3.4: Schematic of plasma etch process to create a patterned silicon substrate.

ure 3.3. This lined substrate was then placed into a Oxford Instruments PlasmaLab System 100 plasma etcher. The silicon was etched using an SF_6 plasma, in which the highly reactive fluorine (F^-) ions react with the silicon substrate. The reaction proceeded with an etch rate of 100 nm/min.

3.1.6 PDMS Fabrication

In Chapter 4, UV lithography followed by plasma etching was used to create trenched silicon moulds, which were treated with octadecyltrichlorosilane (OTS) prior to stamp production in order to facilitate easy removal of the PDMS from the mould. OTS acts as an anti-sticking agent by forming a self-assembled monolayer on the silicon surface, which alters the surface energy such that the PDMS does not strongly adhere to the surface.^{62,63} In order to assemble the OTS monolayer, the mould was placed in a 5 mM solution of OTS in toluene for 2 hours. The mould was then rinsed in toluene and dried with N_2 . PDMS was mixed with its cross-linker in a 10:1 ratio and placed in low vacuum (0.01 - 0.1 bar) for one hour to remove air bubbles. The PDMS was then poured over the mould and cured at 100 °C for 1 hour. Upon cooling, the PDMS stamp was peeled off. This process is depicted in Figure 3.5.

In Chapter 7, the mould for the PDMS consisted of a plastic mould made using a 3D printer. After pouring the PDMS over this mould, it was left to

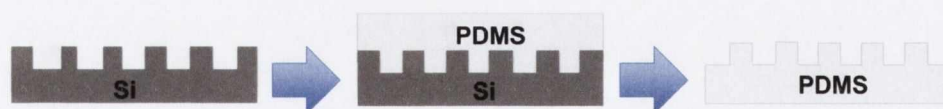


Figure 3.5: Schematic of PDMS stamp fabrication process. (a) Trenched silicon mould. (b) PDMS is poured over mould and cured then (c) peeled off. This creates a trenched PDMS stamp.

cure in air for 24 hours. Heat treatment was not applied as it could damage the plastic mould. After 24 hours, the PDMS cell was removed by peeling.

3.2 Characterisation Techniques

3.2.1 Raman Spectroscopy

In this thesis, all Raman spectra and maps were acquired using a Witec alpha300 Raman system equipped with a 532 nm laser excitation source. In Chapter 4 the laser intensity was set to a low value of 0.2 mW for samples with polymer substrates in order to prevent burning of the polymers. For samples in remaining chapters the laser intensity was approximately 0.8 mW. Spectra were recorded using a 600 lines mm^{-1} spectrometer grating.

For scanning Raman spectroscopy, a piezoelectric stage was used to move the sample in the x and y directions and a spectrum was taken after every step. Step sizes were typically between 300 - 400 nm. Maps were constructed from the corresponding spectra using WiTec Project software.

3.2.2 Scanning Electron Microscopy

In Chapter 4, SEM images of graphene on a polymer substrate were obtained using a Zeiss Ultra field emission SEM with a low accelerating voltage (1-2 kV) in order to avoid damage to the polymer. An InLens detector was used for all images. Specific details of the voltage parameters accompany each image.

3.2.3 Atomic Force Microscopy

All AFM data was acquired using an Asylum MFP-3D AFM in tapping mode. Silicon probes were purchased from Budget Sensors with a resonant frequency of approximately 300 Hz and a tip radius of 50 nm. Line profiles were extracted using WSxM software⁶⁴ and plotted in Origin Pro 8.5.

3.2.4 Cyclic Voltammetry

The electrochemical characteristics of graphene samples were investigated using a Gamry Instruments Reference 600 potentiostat in a three electrode configuration. The graphene samples were contacted by sputtering 60 nm Au contacts onto the graphene film using a Gatan Precision Etching and Coating System.

Cyclic voltammetry was conducted using the graphene samples as the working electrode and a platinum wire as the counter, with an Ag/AgCl reference electrode. Samples were placed in a Teflon holder which exposed a circular region of the sample (5 mm radius) to the electrolyte and allowed it to be employed as the working electrode in the electrochemical cell. A 0.1 M aqueous solution of potassium chloride was used to conduct background electrochemical scans.

3.2.5 Scanning Tunnelling Microscopy

The STM images presented in this thesis were acquired by Dr. Nina Berner in collaboration with Prof. Attilio Cafolla in Dublin City University. STM measurements were performed in UHV (pressure below 10^{-10} mbar) at room temperature on an Omicron Variable Temperature (VT)-STM. Tantalum wire was used to attach the samples to tantalum sample plates, which also

helped to ensure electrical contact between the graphene film and the sample plate. The STM tips were electrochemically etched from tungsten wire (0.15 mm diameter) using 2 M potassium hydroxide. The imaging parameters used for each image displayed are provided individually with every figure. The images underwent minimal processing steps limited to FFT-supported flattening and Gaussian blurs (over 2 px) using the software WSxM.⁶⁴

3.2.6 X-ray Photoelectron Spectroscopy

X-ray photoelectron spectroscopy was performed by Dr. Nina Berner. Spectra were acquired under ultra-high vacuum conditions (below 5×10^{-10} mbar), using monochromated Al K α X-rays (1486.6 eV) from an Omicron XM1000 MkII X-ray source and an Omicron EA125 energy analyser. Data analysis was conducted using CasaXPS software.

3.2.7 Water Contact Angle

Water contact angles were measured by dropping a small amount of liquid (2-3 μ L) onto the sample and taking a picture of the side-view. The contact angles were measured using the Contact Angle plugin for the image processing software ImageJ.

3.2.8 Fluorescence Measurements

The fluorescence experiments presented in Chapter 5 were conducted by Dr. Izabela Kaminska from the group of Prof. Sebastian Mackowski at Nicolaus Copernicus University, Torun, Poland. Fluorescence images of bacteria in Chapter 7 were acquired using the microscope in Prof. Martin Hegner's lab in CRANN.

Fluorescence Microscopy

In Chapter 5, fluorescence images were measured with an inverted fluorescence wide-field Nikon Eclipse Ti-U microscope equipped with an Andor iXon Du-888 EMCCD detector. An immersion objective with magnification 100x (Plan Apo, Nikon) and numerical aperture 1.4 was used, which provides spatial resolution of about 300 nm. An LED illuminator (480 nm) equipped with a bandpass filter (FB 480-10) was used as the light source. The excitation power was equal to 100 μ W. Fluorescence emission was extracted by combining a dichroic mirror (Chroma 505dcxr) and a bandpass filter (Thorlabs FB 655-40). Fluorescence intensity maps were collected with or without the electron multiplying gain of 100x and acquisition times from 1s, depending on the experimental conditions.

In Chapter 7, fluorescence images were collected using an Olympus BX51M fluorescence microscope equipped with an Olympus XM10 camera. Excitation light from a 100 μ W halogen source was passed through a U-MNG2 fluorescence mirror unit containing a 530 - 550 nm excitation filter, 570 nm dichroic mirror and a 590 nm emission filter.

Fluorescence Spectroscopy

Spectrally- and time-resolved fluorescence measurements were performed using a home-built confocal fluorescence microscope. The sample was placed on a piezoelectric translation stage, which enabled continuous movement of the sample with respect to the excitation laser beam. Pulsed laser excitation at 485 nm with a repetition rate of 20 MHz and power of 10 W was used.

Chapter 4

Structured Graphene

4.1 Introduction

This chapter details the production of three-dimensional folded graphene structures supported by a polymer scaffold. These structures are formed by deposition of graphene onto a PDMS stamp patterned with trenches followed by spincoating of PMMA and printing of the structures onto a SiO₂ substrate. The effect of strain on the graphene due to different trench depths on the PDMS stamps is evaluated using scanning electron microscopy. The final printed structures were investigated for the presence of strain within the graphene using Raman spectroscopy. Electrochemical measurements were conducted to investigate the effects of an increased surface area due to the folding of graphene.

4.1.1 Graphene wrinkles and folds

It was initially believed that 2D materials would not be stable at room temperature due to thermal fluctuations.¹ With the discovery of isolated graphene sheets, this belief was called into question as graphene was consid-

ered to be completely flat. However, it was discovered that wrinkles and folds do naturally form in the material and are the cause of its stability.⁶⁵ The size of these features ranges from less than 1 nm to tens of nanometres.⁶⁶ Wrinkles have been observed in both mechanically exfoliated and CVD graphene.⁶⁷ Certain bends are seen as intrinsic to graphene, particularly those in samples prepared by micromechanical cleavage. CVD samples also contain these intrinsic ripples, while other folds are produced during cooling after growth due to the difference in the thermal expansion coefficients of graphene and the growth substrate.^{68,69} Further wrinkling can also be induced during the transfer process from the metallic to the insulating substrate; however, it has also been shown that, depending upon the transfer medium, wrinkles in the graphene sheet can also be released.³⁹ There have also been indications that floating a polymer/graphene film in water for a prolonged period of time could lead to the release of folds from the CVD graphene surface.⁷⁰

As graphene is only one atom thick, it is extremely sensitive to changes in its structure. Bends in graphene have been shown to alter its electronic and chemical properties.⁷¹ Scanning tunnelling microscopy studies and electrical transport measurements have revealed that wrinkled areas have a lower conductance, and limit the charge mobility of a graphene crystal. The presence of folds has also been theoretically⁷¹ and experimentally⁷² shown to increase the chemical reactivity of graphene. Wrinkles in graphene are more easily functionalised, thus they can act as blueprints for the selective functionalisation of graphene areas.

Although graphene's electrical properties can be interesting for fundamental research and in some applications such as sensors, the lack of bandgap limits graphene's potential for semiconducting devices. It has been shown that a bandgap can be opened in graphene by the application of strain.⁷³⁻⁷⁵

The controlled application of strain to a sheet of graphene is an interesting topic of research in order to achieve reliable bandgap opening. Recently, interest has emerged in the application of rippled graphene for producing a bandgap, with theoretical studies indicating that it may be possible,⁷⁵ due to the additional strain placed on atoms in wrinkled regions.

4.1.2 Production of folded graphene

Despite the interesting potential of wrinkles for the manipulation of graphene's properties, the controlled production of folds and wrinkles in graphene remains relatively unexplored. The formation of bends by depositing graphene over a flat substrate patterned with silica nanoparticles and subsequent functionalisation of these bends has been demonstrated.⁷² Intentional formation of folds with varying structures (Figure 4.1) in chemical vapour deposited graphene by pre-patterning of the target substrate or the copper growth substrate has been previously reported⁷⁶ along with formation of ripples by thermal annealing in suspended graphene⁷⁷ and ripple formation due to

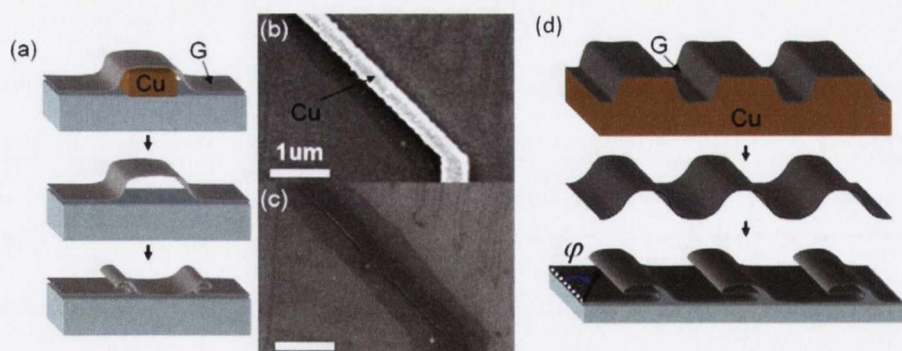


Figure 4.1: a) Intentional folding of CVD graphene by transfer to substrate patterned with copper. b) SEM image of graphene before and c) after removal of copper structure. d) Creation of graphene folds via pre-patterning of copper substrate. Images adapted from Kim *et al.*⁷⁶

buckling in graphene ribbons when placed on a strained elastomeric substrate that is subsequently released.⁷⁸

Transfer printing of graphene

Kinetically controlled transfer printing is a technique that was first demonstrated by Meitl *et al.* in 2006.⁸⁰ A flat PDMS stamp is used to pick up solid objects from a substrate and deposit them onto another. The adhesion and release processes are controlled by the speed of the stamp upon the substrate. Faster speeds are used for object pick-up, while slower speeds result in deposition of the material on the substrate. No specific surface chemistries are required; therefore the objects and substrates can be made of any material. Multiple transfer processes are possible in order to build a three-dimensional structure.^{81,82} Several studies have been conducted on the best way to optimise this process, including the application of shear forces during printing,⁸³ and modifying the structure on the stamp.^{84,85}

A method of producing graphene folds has been developed by Dr. Toby Hallam within the ASIN group utilising kinetically controlled transfer printing.⁷⁹ This method is shown in Figure 4.2 and has been named "GraFold." The process begins with "inking" a patterned PDMS stamp with graphene supported by a polymer layer. As the polymer layer is dissolved, the graphene sinks into the relief patterns in the PDMS. The graphene is then placed in contact with the target substrate. The stamp is peeled back at a slow rate to produce folded graphene. This method produces arrays of free-standing graphene folds which have been investigated for their potential as field emitters.⁸⁶ The method of producing 3D patterned graphene in this chapter is similar, however the graphene is not free standing but supported by a polymer scaffold in order to better control the structures formed.

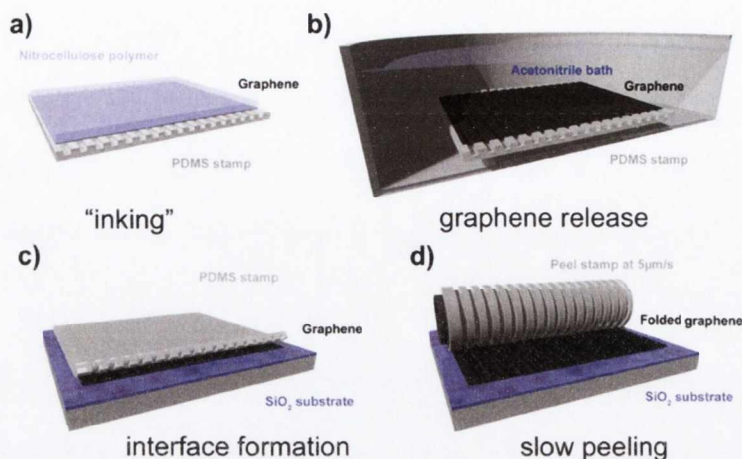


Figure 4.2: Schematic representation of the GraFold concept. (a) A polymer supported graphene film is draped across a relief patterned stamp. (b) Polymer layer is dissolved. (c) The stamp is placed onto the substrate, and PDMS is separated from graphene by slow peeling. (d) Collapse of graphene loops creates free-standing folds. Image from Hallam *et al.*⁷⁹

4.2 Experimental Details

4.3 Standard Graphene Transfer

Flat samples of graphene on SiO_2 are fabricated using the standard transfer process described in Section 3.1.3. In the case of flat samples used for comparison with printed samples, the PMMA polymer was removed using a 4:1 mixture of acetonitrile and ethanol, similar to the folded structures which is described in Section 4.3.1. This was to ensure continuity in sample processing and eliminate any differences due to the use of alternative solvents.

4.3.1 Fabrication of 3D graphene structures

The creation of patterned PDMS stamps is described in Section 3.1.6. These stamps were used in a modified transfer process to create three-dimensional folded structures of graphene. The first steps are similar to the standard graphene transfer process, which has been described in Section 3.1.3. PMMA was spun cast onto graphene grown on copper foils, which were then etched in APS. Using a glass slide, the PMMA/graphene was transferred into deionised water in order to wash away any residue and to ensure complete cleaning of the film. The PMMA/graphene was then transferred to the stamps. Due to the hydrophobicity of PDMS, the typical transfer method of floating the graphene onto a substrate was not possible and an alternative transfer method was devised. A PDMS stamp was placed on the bottom of a shallow petri dish filled with deionised water. A graphene/PMMA piece was floated onto the surface of the water using a glass slide. The deionised water was gradually removed from the dish using a pipette, thus lowering the

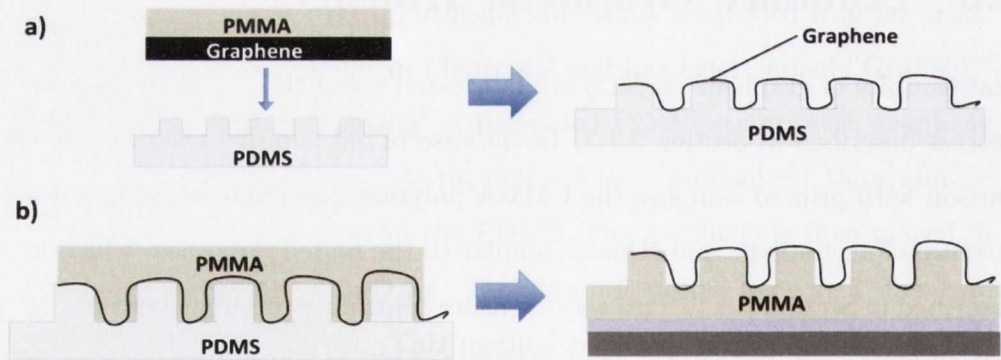


Figure 4.3: Transfer and printing of graphene. (a) The PMMA/graphene film is lowered onto the PDMS stamp and the PMMA is dissolved. Upon drying, graphene conforms to the shape of the stamp. (b) PMMA is spuncast over the graphene and the PMMA/graphene is stamped onto a SiO_2/Si substrate.

PMMA/graphene onto the surface of the stamp. In order to prevent swelling of the PDMS,⁸⁷ the PMMA was then removed using a 4:1 mixture of acetonitrile and ethanol. The stamp was removed from the solution and left to dry overnight. Capillary forces pull the graphene into the trench as the solvent evaporates,⁸⁶ leaving graphene conforming to the surface of the stamp once it has fully dried, as depicted in Figure 4.3(a). A fresh PMMA layer was spun cast onto the stamp (1500 rpm for 30 s) and then printed onto a SiO₂/Si substrate by placing the stamp onto the substrate and peeling it off, resulting in a 3D graphene/PMMA structure as shown in Figure 4.3(b).

The structures were investigated using SEM, AFM, Raman spectroscopy and cyclic voltammetry, details of which are described in Sections 3.2.1 - 3.2.4.

4.4 Results and Discussion

4.4.1 Standard Graphene Growth and Transfer

This short section is intended to convey the quality of graphene produced using the CVD and transfer processes described Sections 3.1.2 and 3.1.3. It also indicates the standard of the graphene used throughout this thesis.

Graphene on copper

Graphene was successfully grown on copper via the CVD process outlined in Section 3.1.2. Graphene nucleation on copper is best analysed using SEM, as Raman spectroscopy on copper foils produces a large background due to localised heating on the substrate, which obstructs identification of the characteristic graphene peaks. Copper foils also tend to have bends which

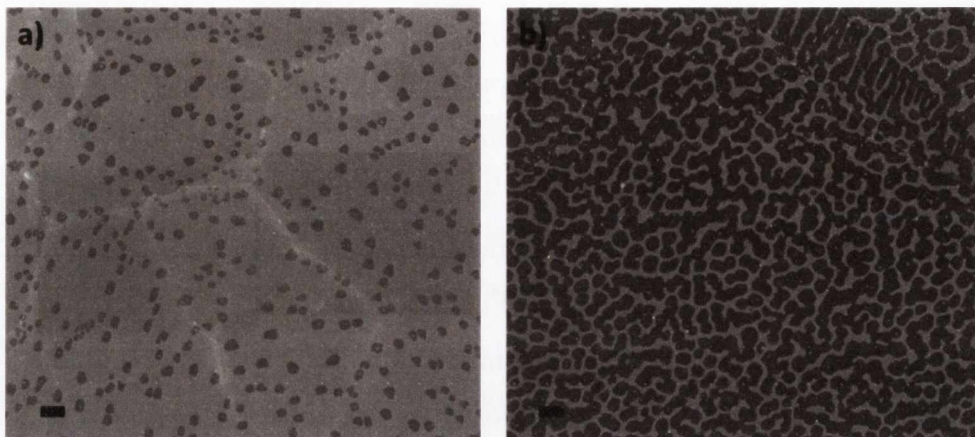


Figure 4.4: a) SEM images of graphene nucleation and b) the merging of graphene domains after 10 minutes of growth. Scale bar is 2 μm . Images were acquired with an in-lens detector and acceleration voltage of 2 kV.

result in an uneven surface that cannot be focused upon over a large area. For these reasons, SEM offers the quickest and most illuminating information on the nucleation and spread of graphene on the copper surface, while Raman is more useful for the characterisation of complete transferred films as the quality of the film can be assessed using peak intensity ratios, as described in Section 2.2.1. Figure 4.4a is a SEM image showing the nucleation of graphene on the copper foil. The dark areas correspond to graphene nucleation sites, while the lighter areas are the copper. Grain boundaries within the copper foil are also visible. Figure 4.4b is an image of a copper foil after 10 minutes of growth. Further nucleation sites have developed and the domains are beginning to coalesce to form a complete film.

Transferred graphene

Figure 4.5a depicts an optical image of the transferred graphene on SiO_2 . The red box indicates the area of the Raman scan. The average Raman spectrum of the graphene contained within the area is shown in Figure 4.5b. The

characteristic G and 2D bands of graphene are also visible, with the sharp 2D peak indicating monolayer graphene. A very small D peak is visible indicating a low level of defects within the film. The D/G peak intensity ratio gives further insight into the presence of defects within the film and is mapped in Figure 4.5c. The D/G ratio over the entire area is less than 0.1, which is indicative of low defect levels in the graphene. The higher intensity areas are attributed to grain boundaries and folds within the CVD graphene film. The 2D/G ratio is mapped in Figure 4.5d. The map shows good uniformity, with a maximum of 2.5, indicating high-quality, single-layer graphene. The lower intensity regions are attributed to the presence of folds,

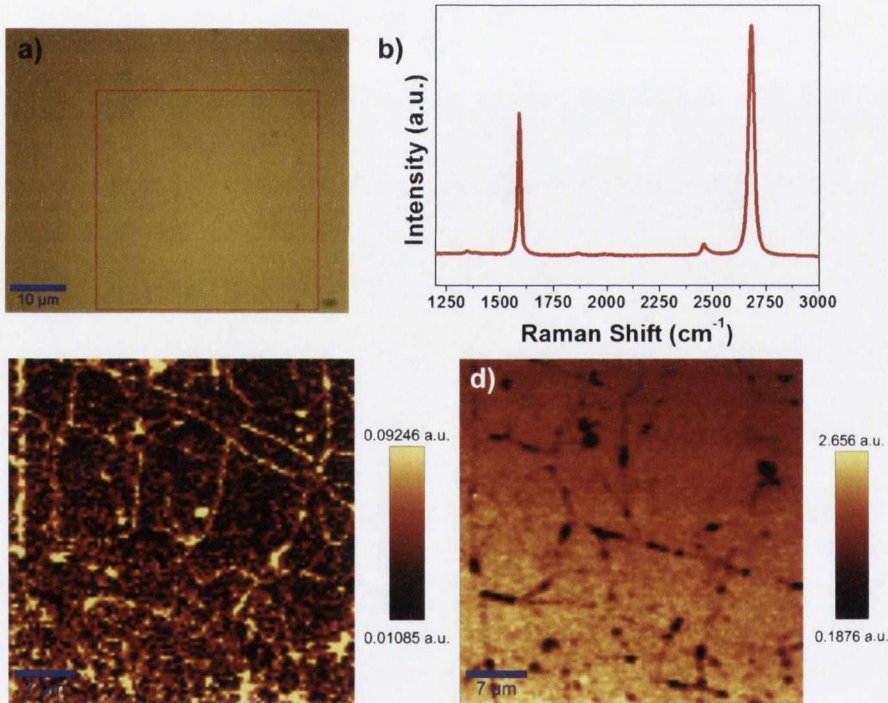


Figure 4.5: a) Optical image of transferred graphene on SiO₂. The area corresponding to the Raman scan region is outlined in red. b) Average spectrum of the graphene contained within scan region. c) Raman map of D/G peak intensity ratio and d) 2D/G peak intensity ratio.

or the onset of second layer growth during the CVD process.

4.4.2 Graphene on PDMS stamps

Flat stamps with no pattern and stamps with trench depths of 40 nm, 150 nm, 300 nm and 1.2 μm were fabricated using the methods outlined in Section 3.1.6. The trenches were 2 μm wide and separated by 2 μm . SEM images of the graphene over the surface of the stamps are shown in Figure 4.6. In the case of the a) 40 nm, b) 150 nm and c) 300 nm stamps, it can be seen that the graphene conforms to the pattern on the stamp. Wrinkling is visible on the 40 nm stamp (Figure 4.6a) but the graphene still remains intact. In the case of the 150 nm and 300 nm stamps, tears in the graphene

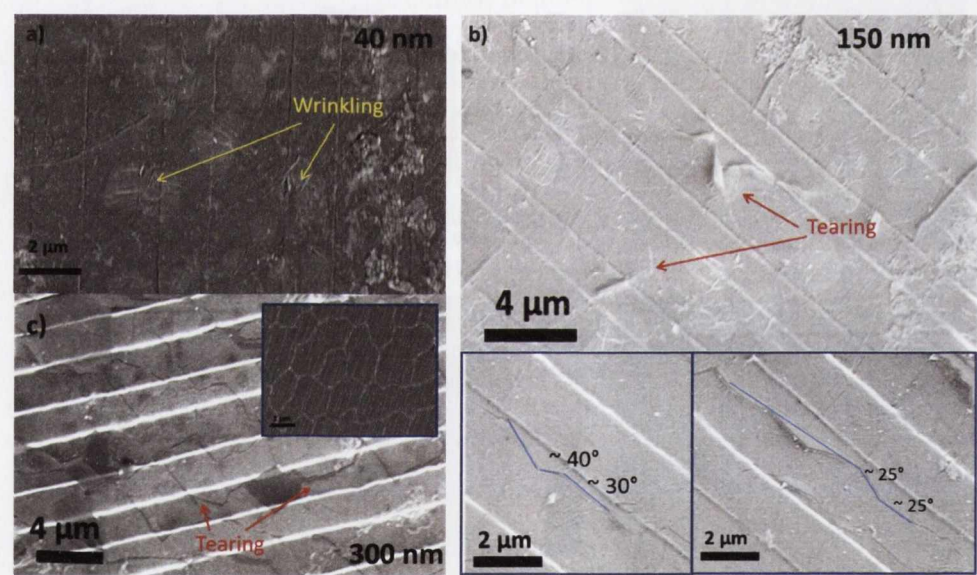


Figure 4.6: SEM images of graphene transferred on to PDMS stamps. (a) Wrinkled graphene on 40 nm stamp. (b) Tearing of graphene on 150 nm stamp, with tearing directions shown below. (c) Unzipping of graphene domains on 300 nm stamp. Inset: outline of graphene domains on copper. All SEM images were acquired with an inlens detector and accelerating voltage of 1 kV.

are visible. For the 150 nm stamp (Figure 4.6b), the graphene is still continuous despite the presence of the tears. It has previously been reported that tearing in graphene propagates along armchair and zig-zag edges, which can be visualised by a 30° change in tearing direction.⁸⁸ A similar pattern of tearing is seen on the 150 nm stamp, as shown in the bottom images of Figure 4.6b.⁸⁸ However, on the 300 nm stamp a different tearing scheme is observed (Figure 4.6c). When the strain is increased due to the change in trench size, separation of the CVD graphene domains is visible. This is confirmed by comparison with an SEM image of incomplete growth on copper foil (Figure 4.6c, inset). The domain shapes are clearly visible and are similar to the shapes on the 300 nm stamp. This change in tearing behaviour can be explained by the increased strain caused by doubling the trench depth from 150 nm to 300 nm. In order to conform to a 150 nm trench, a 7.5 % increase in surface area is required. This is increased in the case of the 300 nm trench to 15 %, resulting in a doubling of the strain experienced by the graphene sheet. The elastic limit of graphene has been calculated to be approximately 20 %, but this can be decreased to 10 % by the presence of defects within the graphene lattice.⁸⁹ In addition, it has previously been reported that the grain boundaries of CVD graphene result in reduced elasticity.^{90,91} Therefore the more pronounced tearing which is observed when the trench depth is increased from 150 to 300 nm is due to the increased strain, which is beyond the elastic limit of the graphene due to the presence of grain boundaries and defects within the CVD film.

When the trench depth is increased to 1.2 μm , graphene suspends across the trenches, with some areas collapsing inside (Figure 4.7a). AFM over the suspended areas shows the graphene sinks 300 nm into the trenches (Figure 4.7b). This indicates that the graphene experiences a high-level of strain

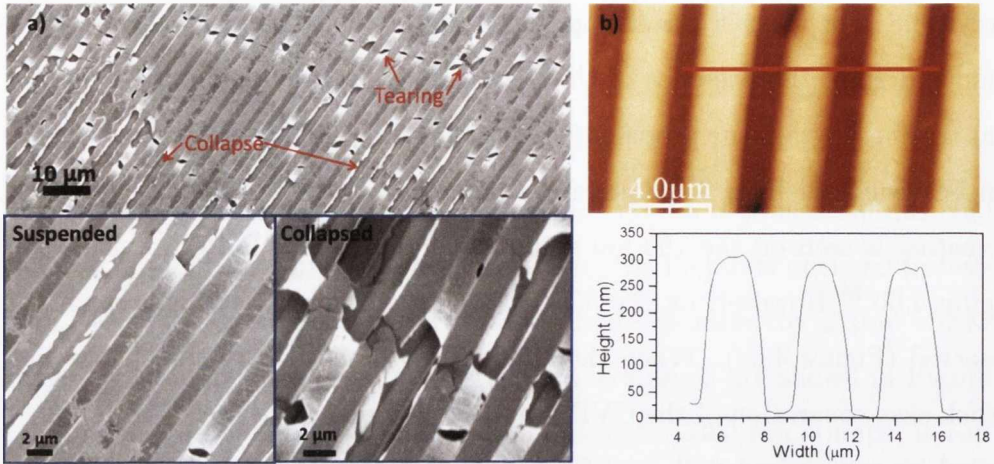


Figure 4.7: (a) Upper: Graphene over 1.2 μm trenches. Lower: Intact graphene and collapsed graphene. SEM images were acquired with an inlens detector and accelerating voltage of 1 kV. (b) AFM image of graphene suspended over trenches, with height profile beneath.

while sinking into the deeper trenches and some areas rupture in order to release tension.

4.4.3 Printed graphene structures

Figure 4.8a shows an AFM image of a 40 nm trench PDMS stamp. The profiles of the Si mould, PDMS stamp and the printed PMMA/graphene structure are shown in Figure 4.8b. The profile of the mould shows a well-defined, sharp morphology. The stamp has a similar morphology, and is the negative of the mould. The dimensions of the printed graphene structure show a good reproduction of the mould. The printed PMMA/graphene structures also show increased roughness due to the wrinkles in the CVD-grown films.

SEM images of printed graphene over PMMA with trench depths of 40 nm and 150 nm are shown in Figure 4.8c and d, respectively. The sample

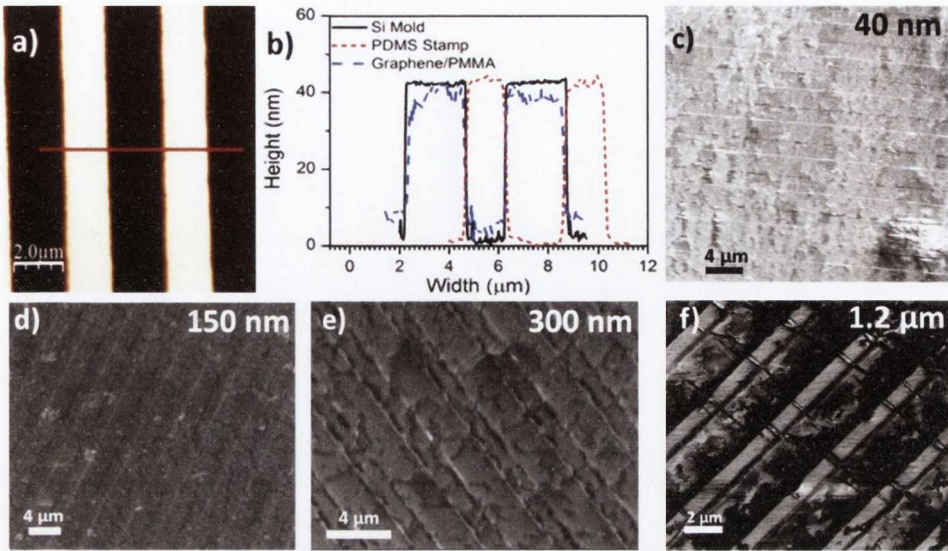


Figure 4.8: (a) AFM image of 40 nm trench PDMS stamp. (b) Profiles of the 40 nm Si mould, PDMS stamp and printed PMMA/graphene structure. (c) - (f) SEM images of printed graphene over PMMA trenches of 40 nm, 150 nm, 300 nm and 1.2 μm , respectively. The sample stage was tilted 45° for the 40 nm, 150 nm and 300 nm samples. Images were acquired using an InLens detector and accelerating voltage of 1 kV.

stage was tilted at 45° for these samples. The trenched pattern visible in this image indicates that the graphene conforms to the shape of the PMMA scaffolding, which is in agreement with what was previously observed on the PDMS stamps. Figure 4.8e shows an image of the graphene printed with a trench depth of 300 nm. Some tears and roughness along the edge of the trenches are visible. This is attributed to the tearing behaviour that was observed on the PDMS stamp.

Graphene at the tops of the trenches is not visible in the SEM image of the printed 1.2 μm structures shown in Figure 4.8f. From the SEM image of graphene on the 1.2 μm stamp (Figure 4.7d), it can be seen that the graphene either collapses into the trenches, or remains suspended across them. When PMMA is spun over the graphene, it breaks the graphene film and sinks into

the trenches. When the PMMA structure is subsequently stamped, it results in the pattern seen in Figure 4.8f, where graphene is on the bottom of the trenches but only PMMA is at the top.

4.4.4 Raman Spectroscopy

Figure 4.9a displays a typical Raman spectrum of graphene on the different substrates. On SiO_2 (black line), the G and 2D peaks are located at 1581 cm^{-1} and 2666 cm^{-1} , which are similar to accepted values for graphene on SiO_2 .⁹² The polymer samples show a blueshift of 8 cm^{-1} in the G and 14 cm^{-1}

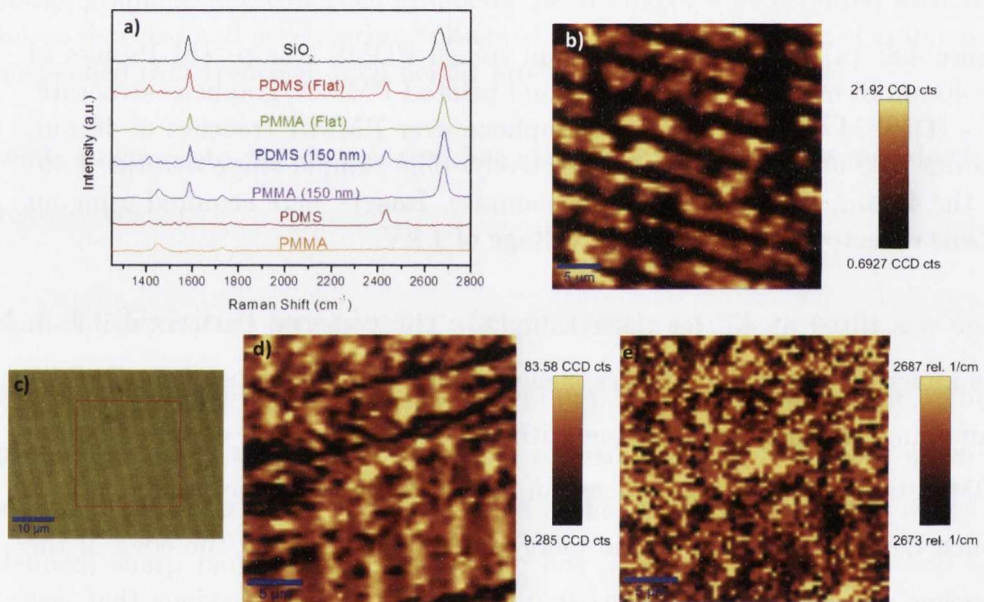


Figure 4.9: (a) Raman spectra of flat graphene on SiO_2 , PDMS, and PMMA and 150 nm trenched graphene on PDMS stamp and PMMA structure. Reference spectra of PDMS and PMMA are also shown. (b) Raman map of 2D peak intensity for a $1.2\text{ }\mu\text{m}$ trench sample. (c) Optical image of graphene/PMMA structures. The outlined area corresponds to the region of the Raman map. (d) 2D intensity Raman map of graphene over 40 nm trenches. (e) 2D peak position on 40 nm sample.

in the 2D peak on PDMS and PMMA, for both flat and trenched samples. The graphene 2D peak on PDMS has previously been reported to blueshift by approximately 15 cm^{-1} due to strain from ripple formation; however no shift in the G peak was observed.⁷⁸ If there was any strain in the folded graphene structures, additional shifts would be expected in comparison with graphene on flat substrates. As no further peak shifts are visible in the structured graphene samples, the shift in the Raman spectra of the structured samples is attributed to hole-doping due to the polymer beneath the graphene.^{37,50} Additional peaks in the spectra of graphene/polymer samples are due to the polymers, as seen in the Raman spectra of pure PDMS and PMMA. The lack of strain in the folded structures is in agreement with what is observed on the SEM images in Figure 4.7, where the graphene releases strain by tearing or unzipping its domains during the drying process on the stamp. Raman maps of the 2D peak of $1.2\text{ }\mu\text{m}$ and 40 nm samples further corroborate with what is observed in the SEM images. Figure 4.9b shows a Raman map of 2D peak intensity over a $1.2\text{ }\mu\text{m}$ trenched sample. The dark regions correspond to the tops of the trenches where the graphene was torn during the stamping process. Figure 4.9c shows an optical image of the structures of graphene over PMMA, the outlined region corresponds to the area shown on the Raman map. Figure 4.9d shows a Raman map of the 2D peak intensity for a 40 nm trenched sample, demonstrating the continuity of the graphene over the structures. The light and dark regions correspond to the top and bottom of the trenches. Raman mapping of the position of the 2D peak also shows no shifts in relation to the trench edges (Figure 4.9e), verifying that there is no additional strain in the structure due to folding.

4.4.5 Electrochemical Characterisation

In order to assess the increase in surface area due to folding of the graphene over the PMMA structures, cyclic voltammetry in KCl background electrolyte was conducted using the graphene samples as the working electrode and a platinum wire as the counter electrode. Cyclic voltammograms of unstamped flat graphene on SiO₂, stamped flat graphene, 40 nm trench, 150 nm trench and 300 nm trench samples of graphene over PMMA in background electrolyte of 0.1 M KCl at 20 mV s⁻¹ are shown in Figure 4.10. The charging currents have an unusual asymmetry, diverting from the usual rectangular shape expected for only capacitive charging. This shape did not change over the course of 300 cycles. This shape has been observed previously in monolayer graphene⁹³⁻⁹⁵ and has been attributed to poor contacting

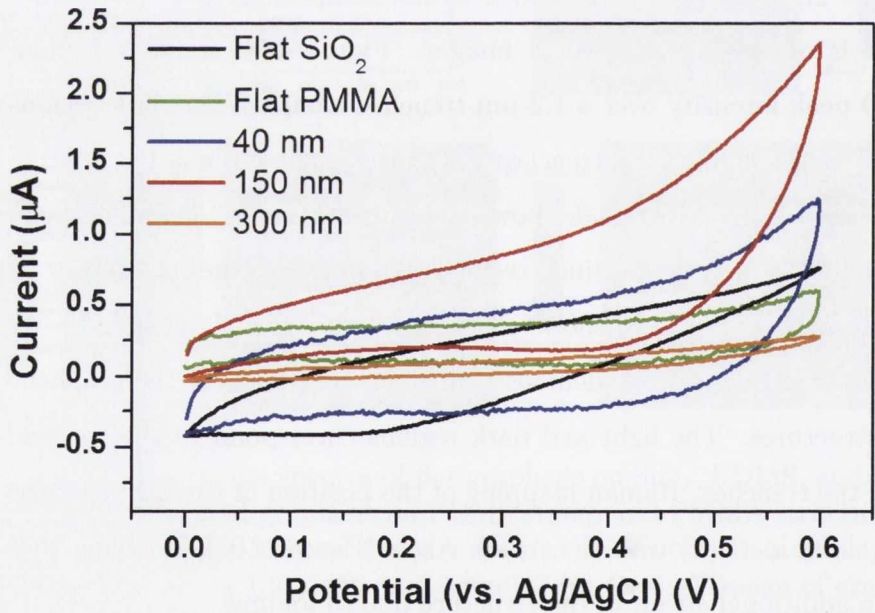


Figure 4.10: Cyclic voltammograms of graphene samples in 0.1 M KCl. Scan rate: 20 mV s⁻¹.

of the graphene film.⁹³ The graphene samples are connected to the circuit *via* an alligator clip, which may introduce additional resistive components into the system by damaging the graphene film.

The 40 nm and 150 nm trenched samples show an increase in charging current in comparison to the flat samples with the highest current observed for the 150 nm trenches. The lower current for the 300 nm sample is attributed to the unzipping of the graphene domains on the stamp, leading to isolated patches of graphene that are unable to conduct current to the contact. The increase in current for structured samples in comparison to flat graphene can be attributed to an increased surface area, as described in Section 2.2.4. This is in agreement with the SEM images of the printed structures, where continuous graphene films were observed for the 40 and 150 nm samples. Although some tearing in the 150 nm samples occurs, these measurements indicate that it does not negatively influence the continuity and conductivity of the graphene. It must be noted that these measurements highlight the ability of the graphene films to conduct current, despite the folding and tearing during the transfer process. Even highly damaged 300 nm films still maintain some current-carrying ability.

4.5 Conclusions

The ability to structure graphene using a patterned PDMS stamp in a soft lithographic process has been demonstrated. The behaviour of the graphene on the stamps after the drying process has been investigated and differing tearing regimes dependent upon the trench depth have been observed. For 40 and 150 nm trenches, the graphene film remains intact with some wrinkling and tearing occurring. For 300 nm trenches, the domains of the CVD

graphene begin to unzip due to the strain as the graphene is pulled down the trench. In the case of 1.2 μm samples, the graphene demonstrates two types of behaviour: folds into the trench to a depth of 300 nm, where it remains suspended, or collapsing into the trench.

The final printed graphene/polymer structures have been investigated structurally and electrochemically. Atomic force microscopy shows the ability of the stamped graphene to reproduce the pattern from the master mould. SEM images indicate that the printed structures replicate the behaviour of the graphene on the PDMS stamps. This is confirmed by Raman maps of the printed structures. Strain in the graphene is not observed in the Raman spectra and this is attributed to the release of strain by tearing and unzipping of the graphene domains upon drying on the stamps. Electrochemical measurements demonstrate that the graphene is electrically conducting even after transfer. Cyclic voltammetry in background electrolyte indicates an increased surface area due to the structuring of the graphene, with the current level increasing from flat to 150 nm trenched samples. This further indicates the continuity of the graphene over the surface of the trenches, as observed by SEM and Raman spectroscopy. The lower current levels for the 300 nm trenches are also in agreement with the SEM images, which indicated discontinuities in the graphene film due to separation of the CVD grains. These discontinuities lead to isolated areas of graphene that are not part of the circuit.

Chapter 5

Non-covalent Functionalisation of Graphene

5.1 Introduction

This chapter focuses on the introduction of functional groups by non-covalent functionalisation of graphene with a perylene bisimide derivative. The molecule which this research is based on, **1**, is shown in Figure 5.1 and was synthesised by the group of Prof. Andreas Hirsch in Friedrich Alexander University, Erlangen Nuremberg, Germany.⁹⁶ This chapter describes the deposition of **1** and the effects of the graphene surface on the formation of molecular films and the orientation of the molecules.

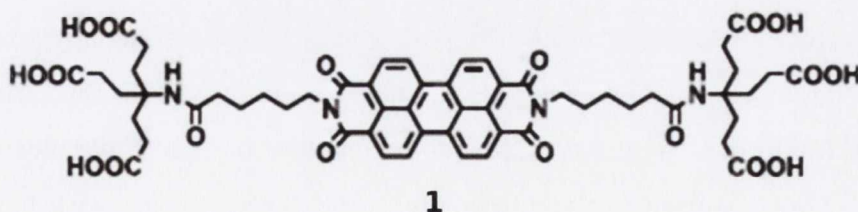


Figure 5.1: Chemical structure of **1**.

5.1.1 Covalent versus non-covalent functionalisation of graphene

Graphene is chemically inert due to its π -conjugated network. While this inertness is an advantage for some applications of graphene, such as in anti-corrosion coatings⁹⁷ and gas barriers,⁹⁸ in others it can be seen as a hindrance. In particular, graphene has been utilised as the active sensing layer in a variety of electronic biosensors.^{15,99,100} However, in order to ensure selectivity of these sensors, it is necessary to introduce specific biomolecules to the graphene surface,¹⁰¹ which is further discussed in Section 7.1.2. Direct functionalisation of the graphene is an option that has been explored,¹⁰² however this method breaks the π -conjugation symmetry of the graphene and has been shown to degrade its properties.¹⁰³ In contrast, non-covalent functionalisation is an attractive strategy to introduce chemical functionalities to the graphene surface as it does not adversely affect the graphene layer.¹⁰⁴ Polycyclic aromatic compounds have been repeatedly reported to adsorb onto graphene *via* van der Waals interactions between the π -conjugated core of the molecule and the graphene, often called π - π stacking.^{105–107}

5.1.2 Molecule deposition methods

The majority of studies on the non-covalent functionalisation of graphene have been conducted on liquid-exfoliated graphene flakes or on graphene grown on SiC substrates under UHV conditions.^{108,109} On epitaxially grown graphene, the molecules are generally thermally evaporated onto the surface in UHV conditions. For liquid-phase functionalisation, the molecules are applied to the graphene surface by mixing a molecule solution with liquid exfoliated flakes. The main focus of the functionalisation of graphene flakes

in liquid is to improve their solubility, particularly in aqueous media.¹¹⁰ The molecule that is the focus of this chapter, **1**, was originally designed for this purpose.¹⁰⁸ However, solution processing of graphene produced by other methods is also of interest due to its scalability, rapidity and operation at room temperature. It also opens the possibilities for a wider variety of molecules to be used, as some higher molecular weight compounds cannot be evaporated due to decomposition at high temperatures.¹¹¹ CVD graphene can be functionalised by both thermal evaporation and wet-chemical processes, as has been demonstrated in a variety of publications.^{112–114} The combination of CVD graphene and liquid-phase functionalisation is very useful as it offers the mass production of high-quality functionalised graphene which can be used in industrial applications, such as coatings, electronic devices and sensors. The molecule deposition methods and the various graphene substrates to which they have been applied is summarised in Table 5.1.

Production Method	Molecule Deposition	References
Liquid Exfoliation	Solution	108, 110
Epitaxial	Thermal evaporation	109, 111
	Solution	111
CVD	Thermal evaporation	111, 112
	Solution	113, 114

Table 5.1: Summary of graphene production methods and molecule deposition techniques used to non-covalently functionalise the graphene surfaces.

5.1.3 Molecular orientation on graphene

Epitaxial graphene

The typical test substrate for studying the orientation and packing of molecules on graphene is epitaxial graphene grown on silicon carbide as the graphene can be made and functionalised without exposure to atmosphere. While a variety of molecules have been studied, the most common is perylene-3,4,9,10-tetracarboxylic dianhydride (PTCDA), which is often used as a model system for describing a polycyclic aromatic compound adsorbing onto graphene. Its structure is depicted in Figure 5.2a. The earliest study of PTCDA was conducted on bilayer epitaxial graphene using a low temperature STM with images obtained at 4.7 K.¹¹⁵ It was revealed that the PTCDA molecules arrange themselves in a brick wall structure across the graphene, with their core perpendicular to the surface, as shown in Figure 5.2b. In the same study, it was found that PTCDA formed a herringbone structure on highly ordered

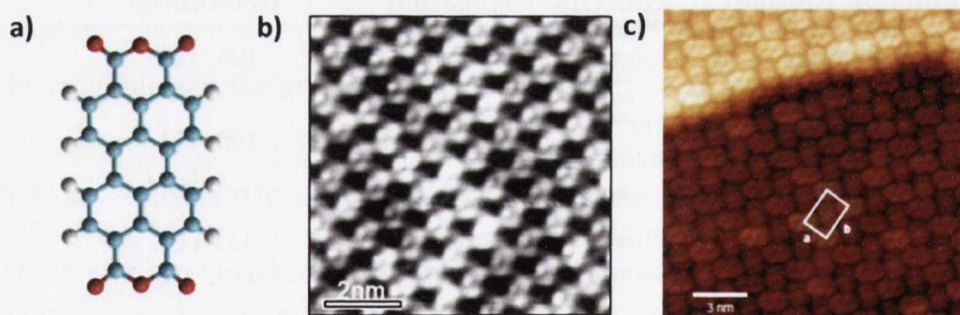


Figure 5.2: a) Chemical structure of PTCDA. Green: C atoms. Red: O atoms. White: H atoms. b) STM image of PTCDA brick wall arrangement on bilayer epitaxial graphene at 4.7 K. c) STM image of PTCDA in a herringbone arrangement on epitaxial graphene at room temperature. The PTCDA molecular structure and outline of the unit cell are overlaid. Figure is adapted from Lauffer *et al.*¹¹⁵ and Wang and Hersam.¹¹⁶

pyrolytic graphite (HOPG) surfaces at the same temperature. This type of molecular arrangement is more typical of PTCDA and had been observed on metal surfaces previously. Later work by the Hersam group on PTCDA layers on monolayer epitaxial graphene revealed the expected herring bone structure at room temperature,¹¹⁶ as depicted in Figure 5.2c. These studies emphasise the importance of the type of graphitic substrate used for the study of self-assembly, as HOPG is often used as a model system for graphene. This paper indicates that the assumption that molecular behaviour is similar on HOPG and graphene may not be valid and can depend on the number of graphene layers present and the temperature of the substrate.

Studies of other aromatic compounds such as phthalocyanines¹¹⁷ also showed a propensity for lying flat on the graphene surface, giving further credence to the accepted view of stronger π - π interactions between the graphene and the molecule than the intermolecular forces at room temperature. Recently, this view has been called under question as Nair *et al.* demonstrated that a tetrathiafulvalene (TTF) derivative adsorbed onto epitaxial graphene in a perpendicular configuration when thermally evaporated and a planar one when deposited from solvent.¹¹⁸ This study indicated that temperature and substrate may not be the only determining factor in the self-assembly of organic molecules, but the role of a solvent (if present) must also be considered. The various orientations of molecules on epitaxial graphene and the conditions under which they were produced is summarised in Table 5.2.

CVD graphene

In the case of CVD graphene, it is also commonly assumed that the molecules adsorb in a planar configuration on the surface due to the large collection of studies showing this behaviour on epitaxial graphene. However, some of

Molecule	Orientation	Conditions
PTCDA	Perpendicular	5K ¹¹⁵
	Planar	Room temperature ¹¹⁶
Phthalocyanine	Planar	Room temperature ¹¹⁷
Tetrathiafulvalene ¹¹⁸	Planar	Thermally evaporated
	Perpendicular	Solution deposited

Table 5.2: Summary of molecule orientation on epitaxial graphene under different conditions.

the previously mentioned studies have shown that the deposition method, the substrate temperature and the number of graphene layers can influence the formation of the molecular films. This implies that many of the studies conducted on epitaxial graphene with molecules evaporated in UHV conditions may not be applicable to similar materials such as CVD-grown graphene. In addition, CVD-grown graphene will contain residues from the PMMA transfer process, which cannot be accounted for when studying epitaxial graphene grown on SiC. Currently, there are very few reports of STM studies of self-assembly of molecules on CVD graphene and those existing are typically conducted while the graphene is still on its copper growth substrate and therefore uncontaminated by polymer.^{120–122} Two studies exist of self-assembly on transferred CVD graphene, in which a planar adsorption geometry for both cobalt phthalocyanine and 1,3,5-tris(2,2-dicyanovinyl)benzene were observed.^{123,124} However, these measurements were conducted at low temperatures (5 K) and did not comment on the effect of the presence of PMMA residues. A recent study on the formation of pentacene films on CVD graphene shed some light on the effect of PMMA residues using various surface techniques such as AFM and near edge X-ray absorption fine structure (NEXAFS).¹¹⁹ On graphene that had just been transferred to a

SiO₂ substrate, the pentacene molecules assumed a perpendicular configuration due to the disruption of the π - π interaction between the pentacene and the graphene by the presence of the PMMA residues. When pentacene was evaporated onto graphene that had been annealed to remove the residues, the pentacene sat parallel to the graphene as the molecule-substrate interactions were increased. The two different orientation effects are depicted in Figure 5.3. Further evidence for the disruption to the self-assembly process by PMMA residues was provided by Kratzer *et al.* when they used AFM to characterise the deposition of para-hexphenyl (6P) onto transferred CVD graphene.¹²⁵ The 6P molecules were evaporated onto the surface and formed needle-like structures. The length of the needles increased as the graphene is cleaned with anneals of increasing temperature prior to 6P deposition, as illustrated in Figure 5.4. The limitation of the length of the needles indicates that intermolecular forces are disrupted by the presence of residual PMMA.

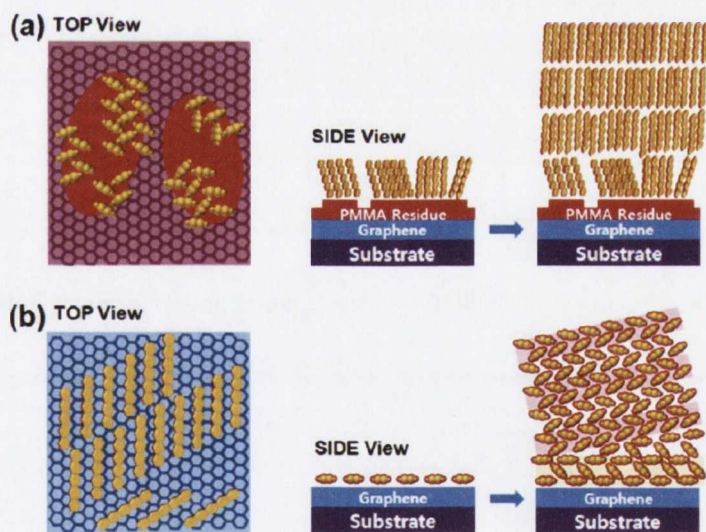


Figure 5.3: Changes in orientation of pentacene molecules (yellow) on CVD graphene for samples with a) PMMA residue and b) no residue. Image adapted from Lee *et al.*¹¹⁹

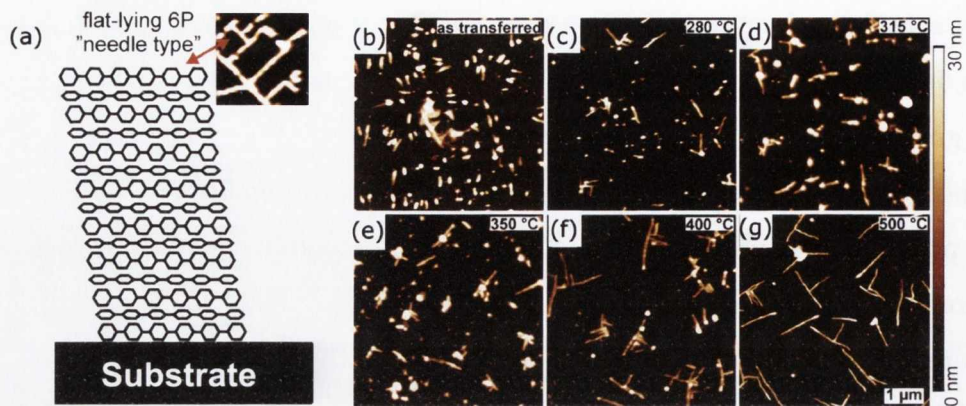


Figure 5.4: a) Schematic depicting assembly of 6P into a needle type structure. Inset: AFM image of 6P needles on graphene. b) - g) AFM images of 6P needle length as it is deposited on PMMA transferred graphene and graphene that has been annealed at temperatures from 280 °C- 500 °C. Figure adapted from Kratzer *et al.*¹²⁵

The orientations of molecules on CVD graphene and the conditions under which they were produced is summarised in Table 5.3.

Molecule	Orientation	Conditions
Phthalocyanine ¹²³	Planar	Transferred graphene, 5K
1,3,5-tris(2,2-dicyanovinyl)benzene ¹²⁴	Planar	Transferred graphene, 5K
Pentacene ¹¹⁹	Planar	Transferred graphene (PMMA residue)
	Perpendicular	Annealed graphene (reduced PMMA)
Para-hexphenyl (6P) ¹²⁵	Short needles	Transferred graphene (PMMA residue)
	Long needles	Annealed graphene (reduced PMMA)

Table 5.3: Summary of molecule orientation on CVD graphene under different conditions.

Intermolecular Interactions

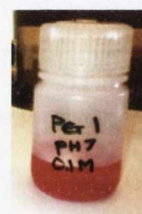
Self-assembly is driven by a range of non-covalent interactions, including van der Waals and hydrogen bonding.¹²⁶ The previous section has focussed on the interaction between the molecules and the substrate; however, intermolecular forces are also important when considering the self-assembly of molecules. For aromatic molecules, π - π interactions between the molecules can be the dominant factor provided they are not disrupted by hydrophobic interactions between long side chains or by steric effects from bulky side chains.¹²⁷ In the case of self-assembly on graphene, if intermolecular π - π interactions are dominant, the molecules must be assembled in a perpendicular configuration and the π - π interaction would occur between the molecules and not the molecule-graphene interface. The majority of studies to date have indicated that the dominant direction of the π -interaction is between the graphene and the molecule.¹²⁸ Therefore the molecular film is stabilised in-plane by other non-covalent interactions. In the case of PTCDA, it has been revealed that the PTCDA molecules are stabilised by a series of hydrogen bonds between the C-O $\cdots$ H-C groups on neighbouring molecules.¹²⁹

As stated in the previous section, the mode of deposition of molecules onto graphene can influence their orientation upon the graphene surface.¹¹⁸ In liquid phase, the molecules interact with each other and with the solvent via non-covalent interactions. In some liquid environments, molecules are not entirely dissociated from one another and can form structures within the solvent. Studies of perylene diimide molecules similar to the molecule used in this chapter have demonstrated self-assembly into nanobelts within solution due to strong π - π interactions between the perylene cores. The molecules remain in this configuration upon spincoating onto a glass substrate, indicating very strong intermolecular interactions.¹²⁹ It is known that the molecule

used within this study, **1**, forms micelles when placed in solution.⁹⁶ Therefore similar strong π - π interactions may dominate self-assembly on solids. As **1** contains carboxylic acid groups, it is likely that hydrogen bonds will form between the functional end groups of the molecules, further increasing the strength of their interactions.

5.2 Experimental Details

Graphene was grown by CVD and transferred as described in Sections 3.1.2 and 3.1.3 in Chapter 3. **1** was dissolved in aqueous sodium phosphate buffer (0.1 M, pH 7) to form a 0.001 M molecule solu-



tion, as shown in Figure 5.5. The solution was dropcast onto the graphene and the samples were subsequently rinsed in deionised water followed by isopropyl alcohol. The molecular layers were characterised by Raman spectroscopy, water contact angle, scanning tunnelling microscopy (STM) and fluorescence measurements which have all been described in detail in Chapter 3 of this thesis.

5.3 Results and Discussion

5.3.1 Molecular packing density on graphene

Raman Spectroscopy

Following the deposition of **1** onto CVD graphene from buffer solution, the molecule layer was investigated through Raman spectroscopy. Figure 5.6 shows a typical Raman spectrum of the molecule layer on graphene. **1** can

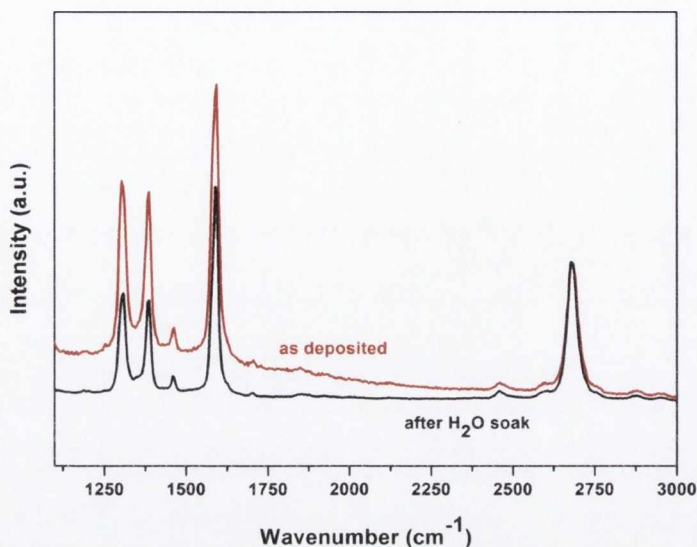


Figure 5.6: Raman spectrum of **1** on graphene after initial deposition (red). The fluorescent background as a result of multilayer formation is visible. After soaking in water, the multilayers are removed and a monolayer remains as observed in the Raman spectrum of rinsed samples (black).

be easily identified by its two main Raman peaks at 1302 cm^{-1} and 1382 cm^{-1} as shown previously by Kozhemyakina *et al.*¹³⁰ on liquid-phase exfoliated graphene flakes. Initially, a fluorescence background in the Raman spectrum due to the formation of a multilayered molecule film on the surface of the graphene (red line) is observed. The multilayers can be removed by soaking the samples in water for 5 minutes, as observed by a reduction in the background on the spectrum (black). The reduced fluorescence background is due to quenching in the presence of the graphene substrate.^{130,131} In multilayered samples, the molecules are further away from the graphene and therefore their emission is uninhibited.

According to Equation 2.1 in Section 2.2.1, the intensity of the Raman signal is linearly dependent upon the number of scattering molecules in a sample. Therefore, if more molecules are present on the surface (i.e. more

densely packed), the intensity of the molecule peaks within the spectrum will be increased. The ratio of the intensity of the **1** peaks to the graphene G peak was utilised to give a qualitative assessment of the packing density of the molecules on the surface. Figure 5.7a depicts an average Raman spectrum of **1** deposited on graphene directly after PMMA transfer (black line). The **1**:G peak ratio is 0.5 and is uniform over the surface as shown in the corresponding Raman map of the **1**:G peak ratio in Figure 5.7b. This map covers a $30 \times 30 \mu\text{m}^2$ area and shows the homogeneity of the molecular layers on the graphene except in areas that correspond to second layer graphene growth. When **1** is deposited on graphene that has been annealed to remove PMMA residues, a much higher packing density ratio of 1.5 is observed, as seen in the blue spectrum in Figure 5.7a and the corresponding Raman map in Figure 5.7b. Additional Raman peaks of **1** are visible in higher density samples, including a peak at 1577 cm^{-1} , which previously was only visible as a shoulder on the

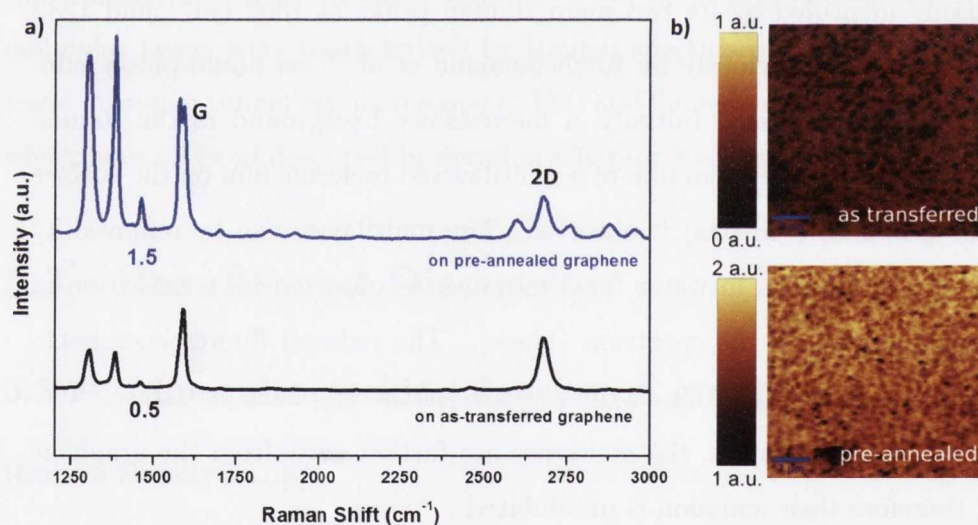


Figure 5.7: a) Average Raman spectra of **1** deposited on as-transferred (black) and annealed (blue) CVD graphene on SiO_2 . b) Corresponding Raman maps of **1**:G peak ratio in low packing density and high packing density layers.

G peak of the graphene. The small peaks around the 2D band are associated with the carboxylic acid dendrimer groups of **1**.¹³⁰

While obtaining the densely packed perylene layers on transferred CVD graphene is very reproducible, the annealing (i.e. cleaning) step takes a long time and represents a bottleneck in the high quality sample preparation process. Therefore, a modified transfer process where the molecules are deposited directly onto the as-grown pristine graphene surface on copper foil before transfer was developed, as shown schematically in Figure 5.8a. This process has been termed functional layer transfer (FLaT).

To produce high packing density samples using FLaT, **1** was dropcast onto the graphene on copper foil and rinsed with water prior to application of the PMMA layer. The presence of **1** on graphene was confirmed with Raman spectroscopy, as shown in Figure 5.8b (inset). The large background and low intensity of the Raman peaks can be attributed to the copper substrate. The sample then underwent the standard polymer-assisted transfer process which has been described in Section 3.1.3. Figure 5.8b shows an average Raman spectrum of the transferred graphene with **1**. A high 1:G ratio of 1.5 is obtained, similar to the packing density after deposition on the transferred and annealed graphene (1.5, Figure 5.7a). The high packing density can be attributed to the cleanliness of the as-grown graphene surface and the molecular film formation is not hindered by polymer residue or other contaminants. Figure 5.8c depicts a Raman map of the 1:G intensity ratio using the FLaT process. The same uniform layer of **1** is observed, indicating that films of **1** that have undergone the FLaT process are not disrupted by the additional processing steps.

The stability of the molecules on the graphene during Raman scanning was tested by exposing the molecules to the laser for several minutes. The

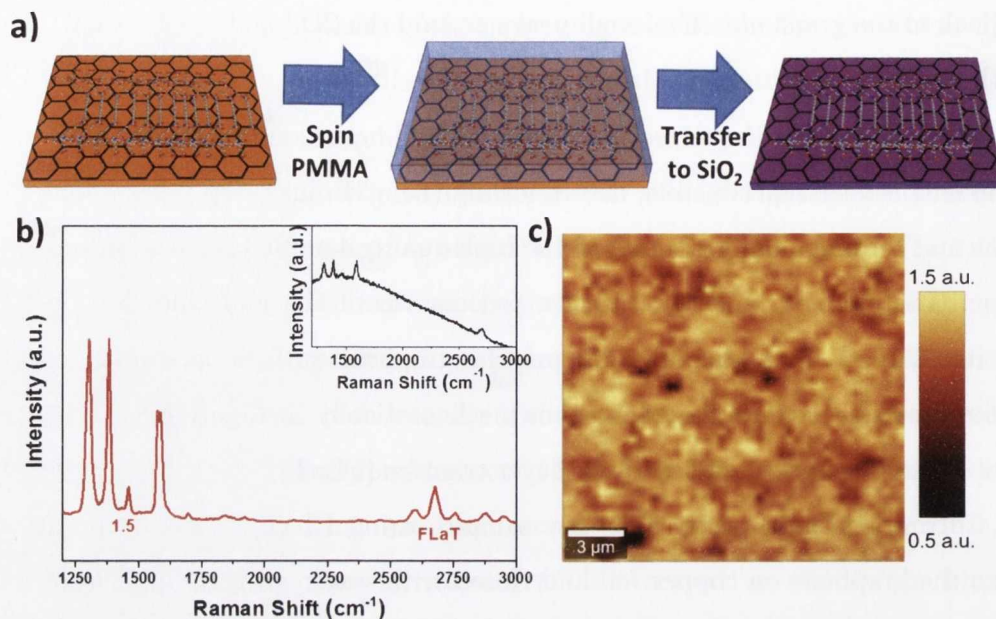


Figure 5.8: a) Schematic of modified transfer process where **1** is deposited onto the graphene on copper before PMMA transfer. b) Average Raman spectrum of **1** on graphene after transfer. Inset: Raman spectrum of **1** on copper before transfer. c) Raman map of **1**:G intensity ratio using this transfer process. The films produced are similar in packing density to the samples made by deposition onto pre-annealed graphene.

molecule films will be removed due to substrate heating if left exposed to the laser on the Raman system for approximately 5 minutes. However, they are not removed during the course of the standard scans displayed in this section. This is due to the low integration time (0.1 - 0.2 s) required for the Raman scans. As stated in Section 3.2.1, the laser intensity was approximately 0.8 mW for all measurements.

Water Contact Angle

The significantly increased packing density of **1** on cleaner graphene is further confirmed by water contact angle (WCA) measurements, typical examples of



Figure 5.9: Water contact angle measurements of a) bare graphene, b) low density **1** on graphene and c) high density **1** on graphene.

which are depicted in Figure 5.9. Bare graphene samples on SiO_2 have a water contact angle of $89^\circ(\pm 1^\circ)$, similar to what has been reported elsewhere.⁵⁷ The contact angle is decreased upon addition of **1** to the surface, due to the presence of hydrophilic groups, in particular the six carboxylic acid functions. For graphene samples with a low packing density of the perylene molecules, a water contact angle of $67^\circ(\pm 2^\circ)$ is measured, while an angle of $58^\circ(\pm 2^\circ)$ is observed at higher packing density of **1**, clearly indicating an increase in the number of carboxylic acid groups on the surface.

5.3.2 Orientation of molecules on graphene

Scanning Tunnelling Microscopy

The exact nature and orientation of the molecular layers is further investigated by STM characterisation of the transferred graphene substrate and subsequent **1** deposition. These measurements were carried out by Dr. Nina Berner in collaboration with Prof. Attilio Cafolla in Dublin City University. Figure 5.10a shows an STM image of CVD-grown graphene transferred with PMMA on SiO_2 before and after an overnight anneal in UHV at 220°C . As clearly visible in the upper part of Figure 5.10a, images taken on the as-transferred surface show streaky features that indicate loosely bound material

which is moved over the surface by the STM tip. In contrast, images taken on the same surface after the overnight anneal are much clearer and show almost no evidence of adsorbates. After deposition of **1** on the pre-annealed, clean graphene substrate and a short anneal to just over 100 °C to remove any adsorbed water, STM images taken over the entire surface area show periodic structures as shown in Figure 5.10b, which, upon closer inspection, can be related to molecular arrays. Figure 5.10c shows line profiles across some of the features which reveal periodicities of 0.23 nm and 3.25 nm along

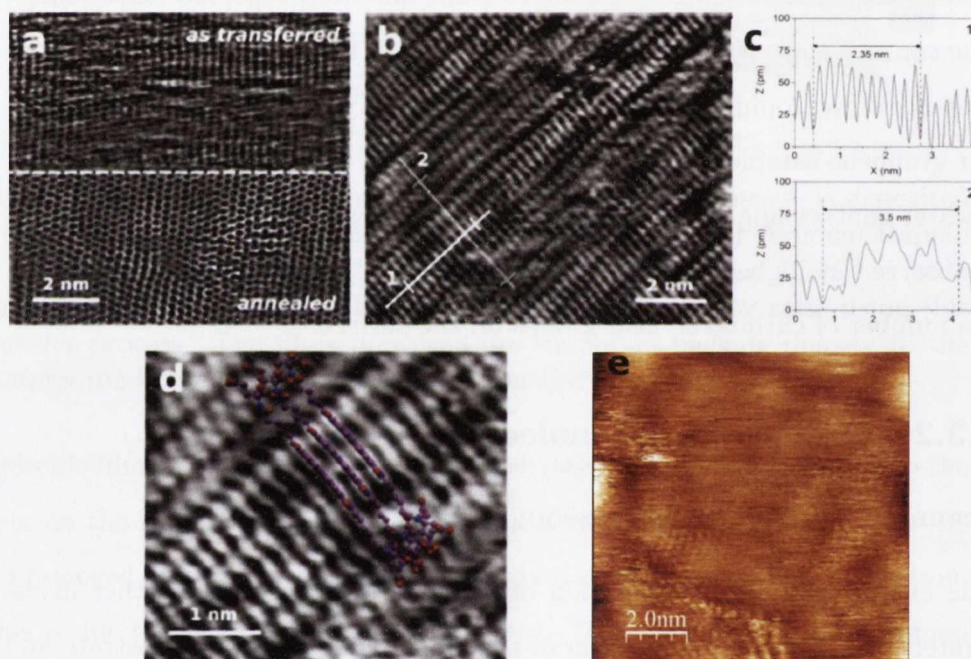


Figure 5.10: STM images of (a) as-transferred (top, taken at -0.3 V/0.3 nA) and subsequently annealed (bottom, taken at -0.5V/0.8 nA) CVD graphene on SiO₂ and (b) after deposition of **1** on the same substrate (taken at -0.5 V/0.1 nA). (c) line profiles from (b). (d) zoomed in area with molecular structure overlay. (e) Typical STM image of low density layers of **1** on as-transferred graphene/SiO₂, with streaky features indicating an abundance of loose material on the surface.

orthogonal directions. This leads to the conclusion that in its high packing density configuration, **1** adsorbs and packs into SAMs with the perylene cores perpendicular to the surface, as indicated by the molecular structure overlay in Figure 5.10d. This observation is in contrast to the common belief that organic molecules with large conjugated π -systems adsorb via π - π interactions between the molecular cores and the graphene substrate, and instead suggests that these densely packed perylene layers are stabilised by molecule-molecule rather than molecule-substrate interactions. These findings emphasise that the adsorption of molecules on surfaces is governed by a complex interplay of interfacial energies between both the molecules themselves and the molecules and the substrate surface. If molecules are deposited from solution, they are surrounded by a much larger number of neighbouring molecules than if they were deposited by thermal evaporation, which changes the energy landscape and therefore the adsorption behaviour significantly. This is particularly the case for **1** which is not present as monomer in solution, but forms micelles due to the strong interaction between the perylene cores and the amphiphilic nature of the molecules.⁹⁶ The other major influencing factor is the surface energy of the substrate, which is evidenced by the difference in adsorption behaviour of **1** when the graphene substrate is contaminated with PMMA residue. In the particular case of the high packing density layer of **1** on clean CVD graphene, it appears that the molecule-molecule interactions are much stronger than the molecule-substrate interactions, but this may be different in an even slightly altered environment, for example by residual PMMA on the substrate. This is indirectly supported by STM images recorded on samples with a low packing density of **1**, an example of which is shown in Figure 5.10e. None of the images showed any clearly resolved features, which indicates an abundance of loose material on the surface and the lack

of molecule-molecule stabilisation in organised structures. Therefore the adsorption geometry is likely to be different for low density films. In fact, the lower density of carboxylic acid groups evidenced by the WCA measurements implies that at least some of the molecules are adsorbed with the perylene core lying flat on the substrate.

Fluorescence Measurements

Although it was not possible to resolve low density layers of **1** with STM, some evidence of vertical packing of **1** on graphene in the low-density packed structure can be deduced from the results of fluorescence imaging and spectroscopy. These measurements were conducted in collaboration with Prof. Sebastian Mackowski at Nicolaus Copernicus University, Poland. Figure 5.11a shows an example of a fluorescence image obtained for a $100 \times 90 \mu\text{m}^2$ area of the sample. While the intensity is rather low, the high sensitivity of the detection system allows for the observation of a fluorescence signal originating from the molecules. Some completely dark areas are visible, but a large fraction of the sample exhibits measurable emission. The overall low emission intensity is a result of both monolayer coverage of **1** on the graphene substrate and energy transfer to graphene. Spectrally-resolved data (Figure 5.11b) obtained for fluorescent regions on the sample provide insight into the molecular arrangement of the molecules as well as the interaction between them and graphene. The emission of the molecules deposited on graphene appears around 670 nm, which is dramatically shifted to longer wavelengths compared to the solution, where the emission maximum appears at 593 nm.¹³² This points towards a strong interaction between aromatic rings of the molecules, which is possible only in a configuration where the molecules are placed at an angle at the surface. Figure 5.11c shows time-resolved data for the monolayer

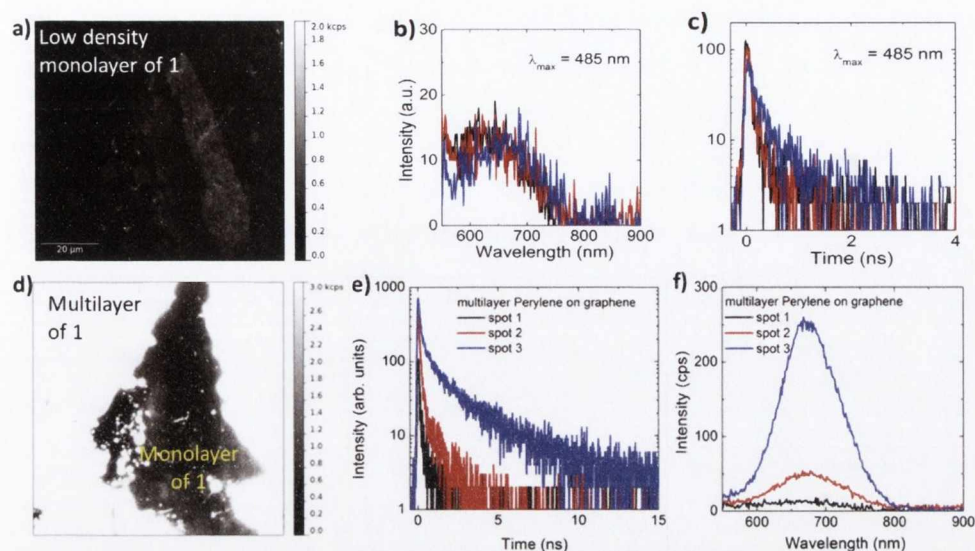


Figure 5.11: a) Wide-field fluorescence image of low packing density **1** on graphene. b) Typical fluorescence spectra and c) fluorescence decay curves obtained for three different locations across the low packing density sample. d) Fluorescence image obtained for samples with areas of multilayer and monolayer coverage of **1**. e) Fluorescence decay curves and e) fluorescence spectra obtained for a sample with multilayer coverage of **1** on graphene for three locations across the sample with different emission intensities. Excitation at 485 nm was used in all experiments.

samples of **1**, which reveal a short fluorescence decay time. In order to assess the percentage of energy transfer in the monolayer samples, a comparison with multilayers of **1**, where the fluorescence is uninhibited, was undertaken. Figure 5.11d is an fluorescence image of a sample containing multilayer and monolayer areas of **1**. Figure 5.11e depicts time-resolved data for multilayer and monolayer regions of **1** on graphene. The decay time for the monolayer region shows a shortening of approximately five-fold in comparison to that of unquenched multilayer **1** areas. Using Equation 2.4 from Section 2.2.6, an energy transfer with a low efficiency of less than 80% can be calculated for monolayer regions, which again suggests that not all of the molecules are ly-

ing flat on the surface, as this would promote essentially complete quenching of the fluorescence.¹³¹ Therefore, it is concluded that for low density monolayer samples, the majority of the molecules are vertical. However some flat-lying molecules may also be present. In addition, the spectral position of high-intensity multilayer regions is exactly the same as for monolayer regions (Figure 5.11d), which further supports that the molecular orientation vertical to the graphene substrate is the most energetically favourable and that molecule-molecule interactions within the same self-assembled layer are the dominating factor, even in multilayers.

5.4 Conclusions

The non-covalent functionalisation of CVD-grown and transferred graphene from aqueous solution has been demonstrated. In addition, an alternative method of introducing organic molecules prior to the polymer transfer process has been developed. Using this method, homogeneous, densely-packed molecule layers can be formed. This FLaT technique is scalable and can be used to produce large areas of non-covalently functionalised graphene while reducing sample preparation time as it eliminates the need to anneal the graphene in order to remove polymer residue and achieve high density films. The dependency of the packing density of perylene bisimide derivative ad-layers on the surface contamination of the graphene substrate has been characterised using Raman spectroscopy and WCA measurements. In contrast to what is usually observed, STM images of densely packed perylene films on CVD graphene reveal a vertical adsorption geometry stabilised by π - π interactions between the cores of the molecules. In lower density films, the altered surface energy of the graphene caused by transfer polymer residue

appears to alter the adsorption geometry of the perylenes and cause them to adsorb with the core flat or at least at a lower angle to the substrate in some regions, while still standing upright in others. This increased understanding of the influence of molecule-molecule and molecule-substrate interactions on the adsorption and self-assembly of organic molecules on transferred CVD graphene is an important step for the application of non-covalent functionalisation of 2D materials.

Chapter 6

Functionalised Graphene Field Effect Transistors

6.1 Introduction

This chapter details the fabrication of graphene field effect transistors (GFETs) and the comparison of behaviour between devices that contain graphene which was functionalised pre- or post-transfer. The functionalisation agent is the perylene bisimide derivative, **1**, that was introduced in Chapter 5. The functionalised devices were tested for gas sensing of ammonia and nitrogen dioxide and compared with the performance of an unfunctionalised graphene device.

6.1.1 Graphene Field Effect Transistors

A field effect transistor consists of source and drain electrodes connected by a channel material and a gate which is separated from the channel by an insulator. The current level in the channel is modulated by application of an

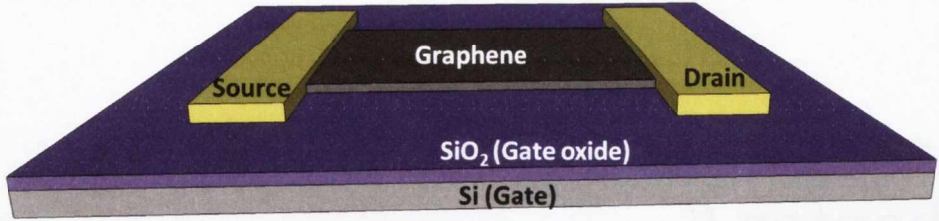


Figure 6.1: Schematic of a typical GFET device, with graphene contacted by metal source and drain electrodes and placed onto a SiO_2/Si wafer. The Si acts as the gate, while the SiO_2 is the gate dielectric.

electric field which is controlled by the gate.¹³³ In a GFET, graphene acts as the channel material and is contacted by metal source and drain electrodes. The most basic back-gated GFET is depicted in Figure 6.1. It is fabricated by placing graphene on a thin (typically 300 nm) silicon dioxide film that covers a heavily doped silicon wafer. The SiO_2 is the gate oxide which electrically insulates the graphene from the heavily doped Si gate electrode. Other architectures for a GFET have been explored such as the use of a top-gate in the form of a dielectric,¹³⁴ and polymer⁵⁰ or solution¹³⁵ electrolytes, but as these device structures were not utilised in this thesis, they will not be discussed here.

Graphene is a semi-metal with no band gap; instead, the valence and conduction bands of graphene meet at a single point referred to as the Dirac point.¹³⁶ As a result of this, GFETs exhibit ambipolar charge carrier behaviour. If the current across the channel is measured as the gate voltage is varied, the type of doping in the graphene can be determined by the location of the point of minimum conduction, or charge neutrality point (CNP).⁵ This is due to graphene's unique bandstructure and is depicted schematically in Figure 6.2. In undoped graphene, the Fermi level, E_F , sits at the Dirac point and the CNP is located at 0 V (red line). If the graphene is p-doped,

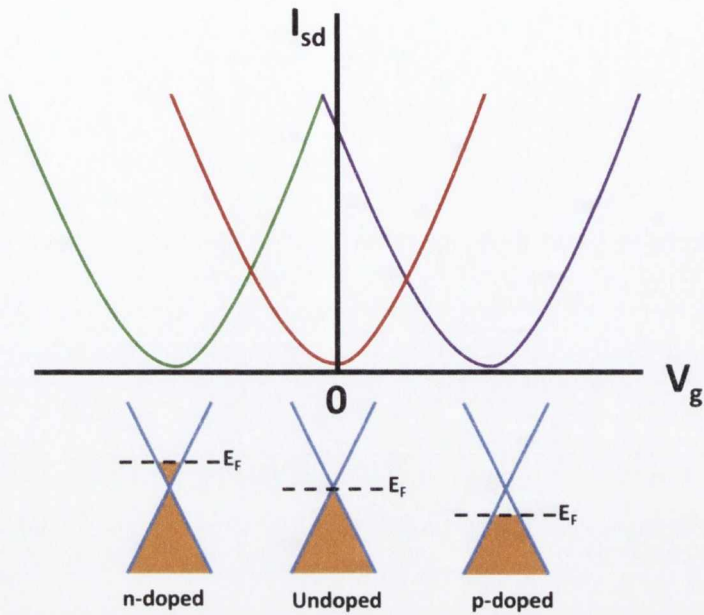


Figure 6.2: Depiction of current vs gate voltage response of a graphene field effect transistor, with corresponding band structure of undoped, p-doped and n-doped graphene.

the Fermi level is shifted into the valence band and the CNP is visible at a positive voltage (purple line). The CNP is at a negative voltage in the case of n-doped graphene (green line).

In ambient conditions, graphene is typically very heavily p-doped and its mobility is reduced due to adsorption of water molecules and scattering from the SiO_2 substrate.¹³⁷ In order to prevent this, different methods of encapsulation have been attempted such as placing boron nitride sheets above and below the graphene in order to reduce interaction with the substrate and prevent doping from the air.¹³⁸ Creating suspended graphene devices by removal of the substrate beneath the graphene channel has also been attempted in order to avoid substrate effects.¹³⁹ In transistors made using CVD graphene, additional p-dopants from polymer contamination due to the transfer process are present, but can be removed following an annealing

process.³⁷

When graphene was first discovered, it was heralded as a replacement for silicon in traditional semiconductor technologies due to its superior mobility at room temperature ($\sim 200,000 \text{ cm}^2/\text{V}\cdot\text{s}$,⁷ in comparison to $1,450 \text{ cm}^2/\text{V}\cdot\text{s}$ for silicon.¹³³) However, the lack of bandgap and therefore the ability to turn off the graphene transistor device is a major hindrance to graphene's mainstream integration. Despite this, GFETs continue to be heavily investigated, especially in areas where the lack of bandgap may not be a problem. In particular, sensor applications where a change in the baseline current is all that is required is a very popular area where it is expected that graphene transistors can be applied in the future.

Functionalised GFETs

The control of the electrical properties and in particular the doping of graphene is an area of high research interest. The functionalisation of graphene has been introduced as a method of controlling the type of doping in the material.¹⁴⁰ Molecules which donate or accept electrons have been placed onto graphene in order to intentionally n- or p-dope the transistor channel.^{141,142} However, recently there have been reports of unreliable and unreproducible shifts in GFET transfer curves due to the interference of solvents when depositing molecules from the liquid phase.¹⁴³ The devices only became stable after annealing in vacuum for over 12 hours. Therefore a method of functionalising graphene that reduces contamination is necessary if liquid phase deposition of molecules is to be employed. Functionalised GFETs have been heavily investigated in gas and biosensing applications.^{144,145} The application of graphene in biosensing will be discussed in Chapter 7, while a short review of gas sensing with graphene will be given in the following section.

6.1.2 Graphene-based Gas Sensors

There are numerous factors that influence the success of a gas sensor. In addition to detecting low levels of specific gases, the device must be able to operate in harsh environments and require low amounts of power.^{146,147} Graphene has been proposed as a potential gas sensing material due to its sensitivity to the environment, chemical inertness, and the low power required to operate devices. The sensing mechanism in graphene based-gas sensors is generally attributed to charge transfer or chemical gating from the gas molecules on the graphene upon adsorption. Schedin *et al.* were the first to report graphene's gas sensing abilities by exposing a micromechanically exfoliated flake to various gases and detecting shifts in the doping levels of the graphene due to charge transfer.¹⁴⁸ They demonstrated that graphene was sensitive down to a single molecule level in the case of nitrogen dioxide. This has led to a large amount of research into the production of gas sensors based on graphene FETs, particularly on the larger scale.^{149,150} CVD graphene has been investigated due to the ability to produce larger areas of graphene, however the sensitivity of these devices has not reached the same level achieved by the first report. Yavari *et al.* reported detection limits of approximately 100 ppb (parts-per-billion) for NO₂ and 500 ppb for NH₃ using transferred CVD graphene.¹⁵¹ Later, Chen *et al.* demonstrated the lowest detection levels of 2.06 ppt (parts-per-trillion) NO₂ and 83.7 ppb NH₃ using CVD graphene by placing the sensor under constant UV illumination.¹⁵² The UV light cleans the graphene surface of adsorbates *in situ* and results in a higher sensitivity of gas detection.

A study by Dan *et al.* compared the sensitivity of lithographically processed mechanically exfoliated graphene with samples that had been annealed

to remove polymer residues from the patterning process.¹⁵³ The cleaned samples demonstrated much lower sensitivities to solvent vapour exposure than that of the samples that had not been annealed. AFM studies revealed that the uncleaned samples had a thin (approximately 1 nm) layer of polymer residue on the surface. This led the group to conclude that the polymer layer acts as an unintentional functionalisation agent on the graphene, which traps the vapours close to the surface and enhances the signal. Thus, in order to achieve increased sensitivity in graphene sensors, a thin molecular ad-layer may be beneficial. In this chapter, the sensing performance of bare graphene will be compared with that of graphene that has been functionalised with **1**. It is expected that the functionalised devices will exhibit higher sensitivity due to the presence of the molecular film on the surface, similar to the previous study. The performance of low and high-density molecule films produced by post-transfer deposition and FLAT will also be compared to assess if the film quality has an impact on the sensing ability of the graphene.

Although pristine graphene gas sensors with high sensitivity have been demonstrated, the issue of selective sensing has not been addressed by the previously mentioned studies. Due to the sensitivity of graphene to its external environment, selective gas sensing with pristine graphene is very difficult and there have been very few studies demonstrating this. One study found that the combination of low-frequency noise measurements in tandem with changes in resistance of a graphene device could be used to selectively detect tetrahydrofuran and chloroform vapours, respectively.¹⁵⁴ Other studies on introducing selectivity focus on functionalisation of the graphene surface with metal nanoparticles or molecules.^{155,156} Graphene devices functionalised with **1** will be used to detect both ammonia and nitrogen dioxide and the response to both gases will be compared. The functional groups of **1** are

carboxylic acid groups, which have not demonstrated selectivity to specific gases. Therefore it is expected that the devices will respond to both gases, but the magnitude of response may be different.

6.2 Experimental Details

6.2.1 Device Fabrication

Devices were fabricated by transferring graphene onto heavily doped n-type Si substrates topped with a layer of 300 nm SiO₂ using the standard transfer process which has been described in Section 3.1.3. Prior to transfer, the graphene on copper was cut into $\sim 5 \text{ mm} \times 1 \text{ mm}$ pieces in order to ensure the graphene strip remained inside the electrode area defined by the shadow mask. After graphene was placed on the substrate, a shadow mask was applied and Ti/Au (10/30 nm) was evaporated onto the substrate to define the electrodes. This resulted in a single graphene strip with several electrodes down its length, which defined 10 devices on each chip, as shown in Figure 6.3. The substrates were supplied with a gold contact on the back of the wafer to act as a gate contact.

Two types of functionalised devices were fabricated: (i) devices where the graphene was functionalised and transferred using the FLaT method and (ii) devices where **1** has been deposited after the graphene transfer process, as described in Chapter 5. In the case of devices that were functionalised post-transfer, only half of the graphene was exposed to **1** in order to allow comparison be-

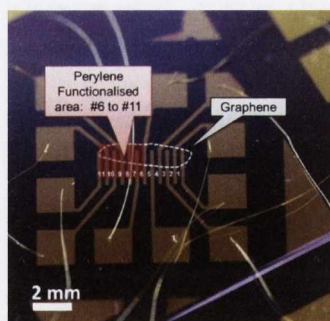


Figure 6.3: Photograph of GFET device.

tween functionalised and unfunctionalised devices. This was achieved by placing a drop of the molecule solution onto half of the devices on the chip using a pipette. The solution was then removed using a pipette and the chip was rinsed in water. An example of such a chip is shown in Figure 6.3.

6.2.2 Electrical measurements

Prior to gas sensing, transport measurements were conducted to assess the electrical characteristics of the functionalised GFETs. Measurements of the devices in ambient conditions were conducted using a Suss probe station. Measurements in vacuum conditions were obtained using a Janis ST-500 probe station equipped with a heating stage which allowed vacuum anneals to be undertaken. All electrical measurements utilised a Keithley 2612A sourcemeter controlled by a LabVIEW program. Samples were initially measured in atmosphere, then loaded into the Janis chamber and left in vacuum (approximately 5×10^{-6} mbar) for 18 hours. After measurement, the devices were annealed at 200 °C for 2 hours and allowed to cool to room temperature before remeasuring. The field effect mobility, μ , of each device were calculated using the equation:¹⁵⁷

$$\mu = \frac{1}{C_{ox}} \frac{L}{W} \frac{\partial I_{sd}}{\partial V_{gs}} \frac{1}{V_{sd}} \quad (6.1)$$

where C_{ox} is the capacitance per unit area of the gate oxide, L and W are the channel length and width of the device, $\frac{\partial I_{sd}}{\partial V_{gs}}$ is the transconductance and V_{sd} is the source-drain voltage. The value of transconductance to use in the equation was determined by plotting $\frac{\partial I_{sd}}{\partial V_{gs}}$ against V_{gs} and finding the maximum.

It must be noted that these measurements are conducted in a two-point

configuration, therefore contact resistance has been included when calculating the mobility values. The inclusion of contact resistance decreases the mobility and as a result of this, the calculated mobilities represent a lower bound for the actual values.

Gas sensing measurements were conducted in a custom-built vacuum chamber. During measurement, ammonia (NH_3) or nitrogen dioxide (NO_2) gasses were injected at different concentrations while mixed with N_2 . The chamber pressure was approximately 200 mbar. The sensor response is determined by the following equation:

$$\frac{\Delta R}{R_0} = \frac{R_{\text{sensor}} - R_0}{R_0} \times 100\% \quad (6.2)$$

where R_0 is the initial resistance of the sensor and R_{sensor} is the measured resistance upon exposure to the gas.

In order to be considered a true sensing response, the signal-to-noise ratio (SNR) must be at least 3.¹⁵⁸ The lowest concentration of gas detected is therefore limited by the SNR of the device response. The experimental limit of detection (LOD) of a device is the concentration at which the signal SNR is 3.

6.3 Results and Discussion

6.3.1 Post-transfer functionalised devices

In order to determine the effect of **1** on the electrical properties of the graphene, transport measurements of GFET devices before and after functionalisation were undertaken. Typical transfer curves for unfunctionalised graphene devices in atmosphere, vacuum and after annealing are shown in

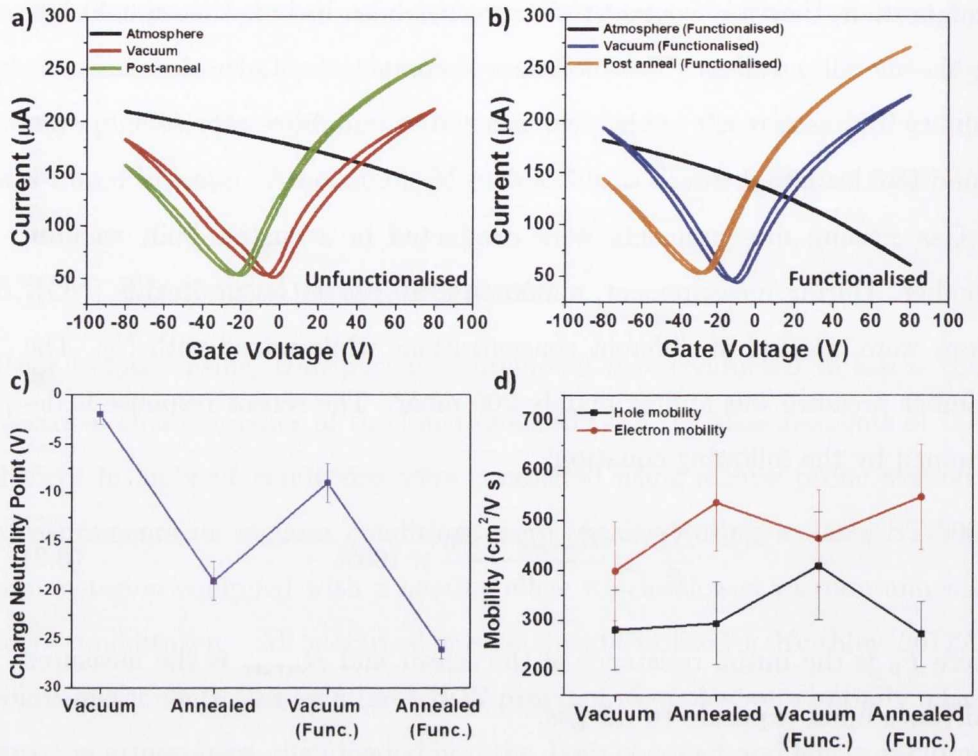


Figure 6.4: Transfer curves for a) unfunctionalised and b) functionalised device in atmosphere, vacuum and after a 200°C anneal. Evolution of the average c) charge neutrality point and d) electron and hole mobilities during the measurement sequence for all functionalised devices.

Figure 6.4a. There is no Dirac point visible in atmosphere. This can be attributed to the presence of a large amount of p-dopants such as water from the surrounding air. These dopants can be removed by placing the device in vacuum, which results in the appearance of a CNP at approximately -3 V. An additional anneal in vacuum shifts the CNP even further negative to -20 V, indicating that the graphene has become further n-doped.

Similar behaviour is observed after the device is functionalised, as seen in Figure 6.4b. Again the measurement in atmosphere indicates that the device is heavily doped despite the previous cleaning. This is due to the fact that

the graphene has been directly exposed to water through the deposition of **1** onto the surface, thus the graphene is heavily doped as a result of this process. Exposure to vacuum moves the CNP to -10 V, which is lower than previously achieved in the unfunctionalised case. After annealing, the Dirac point shifts even further to -27 V. This indicates that the molecules of **1** n-dope the graphene as the position of the CNP is shifted to even more negative values upon exposure to **1**. Figure 6.4c depicts the average CNP for all post-transfer functionalised devices, with the error bars indicating the standard deviation. The same trend as that observed in the individual device is seen for all devices. The average hole and electron mobilities of the devices in each environment is depicted in Figure 6.4d. In both unfunctionalised and functionalised samples, the electron mobility is increased after annealing. In the case of holes, the mobility is greatly increased after functionalisation. However, it is returned to a lower value after the anneal, which indicates that the molecules of **1** do not have a significant effect on the scattering of the charge carriers and the increase in mobility may be due to adsorbants from the molecule solution which are removed during the anneal.

A Raman map of the 1:G intensity ratio measured on the device confirms the presence of the molecules after the anneal, as shown in Figure 6.5a, therefore the decrease in hole mobility cannot be attributed to the desorption of **1**. However, the average spectrum in Figure 6.5b reveals a low 1:G intensity ratio of 0.2, corresponding to very low packing density of the molecules on the surface. Due to this low density, the molecules may have a very limited influence on the mobilities of the GFETs. The molecules do not form a high packing density film on the annealed graphene as they did in Chapter 5 due to the short time of the anneal (2 hours) and the lower vacuum conditions ($\sim 10^{-5}$ mbar) as opposed to overnight in vacuum of $\sim 10^{-9}$ mbar, which

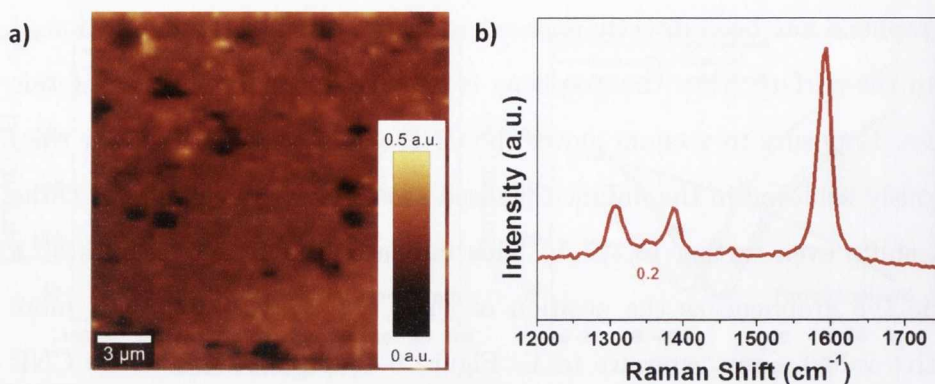


Figure 6.5: a) Raman map of 1:G intensity ratio and b) average Raman spectrum of **1** on device with a low intensity ratio of 0.2. This low value indicates the molecules are not densely packed on the graphene surface.

only partially removes polymer residue from the surface. This observation emphasises the need for very clean graphene surfaces in order to achieve high packing density films of **1**.

6.3.2 FLaT devices

Transport measurements of devices functionalised using the FLaT method described in Chapter 5 were conducted in order to further characterise the effect of the molecules on the device properties. As the molecules are already present prior to device manufacture, exposure of the channel surface to solvent is avoided and therefore the device may present different characteristics. The presence of **1** on the device channel surface after graphene transfer and electrode deposition was confirmed using Raman spectroscopy. The pre-transfer deposited molecular layers are continuous across the surface of the graphene, as observed in the Raman map of the 1:G peak intensity ratio in Figure 6.6a. The molecules are also densely packed, as determined by the 1:G peak intensity ratio of 1.2 from the average Raman spectrum shown in Figure 6.6b. These results coincide with those obtained in Chapter 5 and

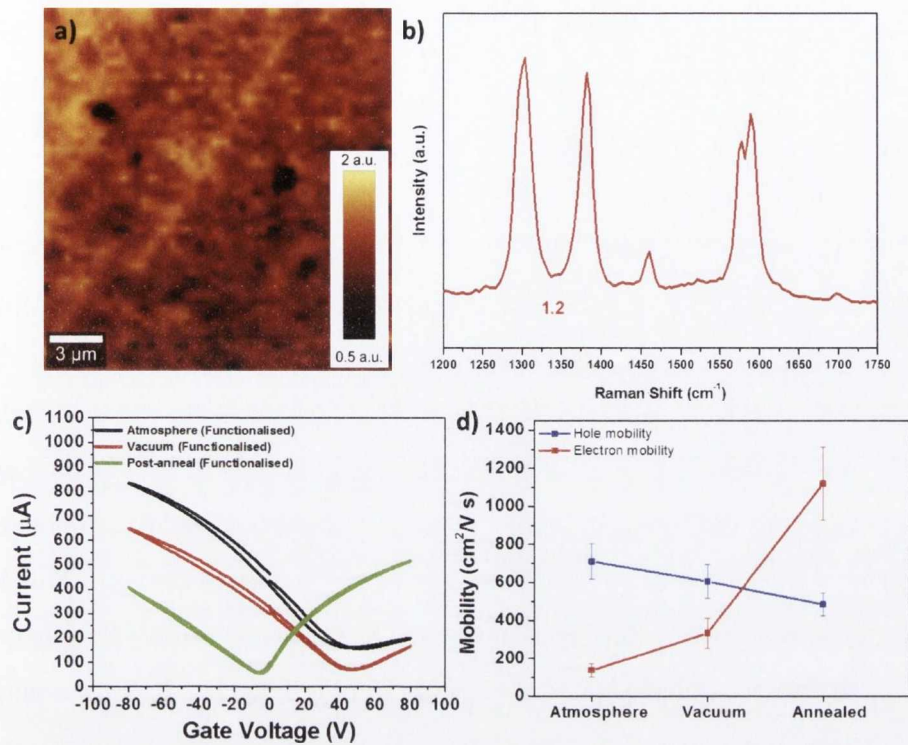


Figure 6.6: a) Raman map of 1:G ratio, indicating homogeneity of the molecular layer across the device surface. b) Average Raman spectrum of the 1 and G band on the device. The peak intensity ratio of 1.2 indicates a densely packed molecular layer. c) Graph of source-drain current vs. gate voltage for pre-transfer functionalised device in atmosphere (black), vacuum (red) and after a 200 °C anneal (green). d) average electron and hole mobilities of all devices during the measurement sequence.

highlight the reproducibility of the FLaT process.

A typical transfer curve for the FLaT devices in atmosphere and after exposure to vacuum and after annealing is shown in Figure 6.6c. In contrast to the devices in the previous section, the CNP is visible in atmosphere, indicating less doping from the surrounding air. This is attributed to the presence of **1** molecules, which encapsulates the graphene and reduces contamination. When placed in vacuum, the CNP is not shifted significantly, further indicating less contaminants on the sample. However, after the anneal the

CNP has moved to -7 V, once again indicating n-doped graphene, which can be attributed to the presence of **1**. There is also a pronounced increase in the electron mobility, while the hole mobility has decreased slightly, which is apparent in the graph of the average electron and hole mobilities in Figure 6.6d. A potential explanation for this asymmetrical behaviour has been described by Farmer *et al.*, who attributed the behaviour to doping within the channel due to the presence of poly(ethylene imine) (PEI) molecules.¹⁵⁹ This doping created asymmetry in the contact resistance at the electrode which suppressed the injection of holes into the channel. In addition, they observed that the reduction in conductance of one carrier (holes) is concurrent with doping due to injection of the opposite carrier (electrons). This is further evidence for the n-doping behaviour of the molecules of **1**. The asymmetry in the carrier injection is visible as the doping from the PEI molecules results in pre-dominantly long-range scattering in the channel, which creates a quasi-homogeneous potential across the graphene. As a result of this homogeneous potential, contact effects are the dominant factor. If there is an inhomogeneous potential across the channel, electrons and holes will be scattered equally, resulting in more symmetrical mobility values as the scattering behaviour in the channel is dominant. As stated in Section 6.2.2 these measurements are conducted in a two-point configuration, therefore contact resistance has been included when calculating the mobility values in this chapter. As a result of this inclusion, the calculated mobilities are reduced and represent a lower bound for the actual values. If the asymmetry is due to the effects that are observed by Farmer *et al.*, the actual mobility value for the holes may be higher, and therefore closer to the electron value and the asymmetry in the calculated values could be purely due to contact effects. In order to determine if the asymmetry in mobility is entirely due to contact

effects, four point measurements should be conducted in future.

The large alteration of mobility is not seen for devices in Section 6.3.1. This could be attributed to a number of reasons: (i) in the FLaT processed samples, **1** molecules are present between the graphene and the metal electrode; this could alter the contact resistance and therefore the carrier injection at the electrode and (ii) the density of the molecules is much larger on the FLaT-processed devices, potentially leading to a higher level of interaction between the graphene and **1**. As seen in Chapter 5, the denser molecule layers are more ordered, which may also provide a quasi-homogeneous potential, leading to effects such as those observed by Farmer *et al.* However, in order to determine the effects of contact resistance, four point measurements are required. In addition, more devices should be produced in order to allow for more rigorous comparison of the mobilities, as the current sample set is limited to 5 devices for post-transfer samples and 10 devices for FLaT samples.

6.3.3 Gas sensing measurements

As stated in the experimental details of this chapter, the post-transfer functionalised chip consists of both unfunctionalised and functionalised devices. This was to allow comparison between the bare graphene and the functionalised graphene during gas sensing measurements. The measurements described in this section were conducted by Dr. Kangho Lee. Prior to measurement, the devices were removed from vacuum before being placed in the gas sensing chamber. As this exposed the devices to atmosphere, the doping level of the graphene may have been altered. As NH_3 and NO_2 are n- and p-doping, respectively, it is necessary to determine the initial doping of the graphene in order to assess the sensing response. Therefore, prior to gas sens-

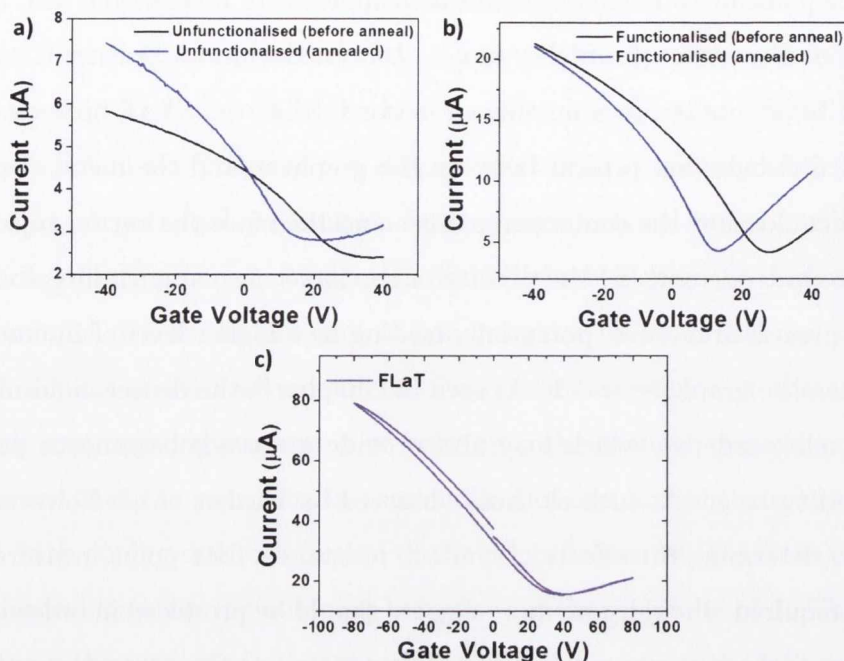


Figure 6.7: Transport characteristics of a) unfunctionalised and b) post-transfer functionalised devices before and after annealing and prior to gas sensing measurements. c) Transport characteristics of FLaT processed device prior to sensing measurements. All devices exhibit p-doped graphene.

ing measurements, the transport properties of the devices were remeasured. Figure 6.7 presents transfer curves of a) bare graphene, b) post-transfer and c) FLaT devices. The position of the CNP indicates that all devices have been p-doped due to their exposure to atmosphere.

Post-transfer functionalised devices

The initial gas sensing response of the unfunctionalised and functionalised samples to a) ammonia and b) nitrogen dioxide is shown in Figure 6.8. The presence and concentration of the gas is indicated by the dashed grey lines. There is a small response by both types of device to the presence of 200 ppm

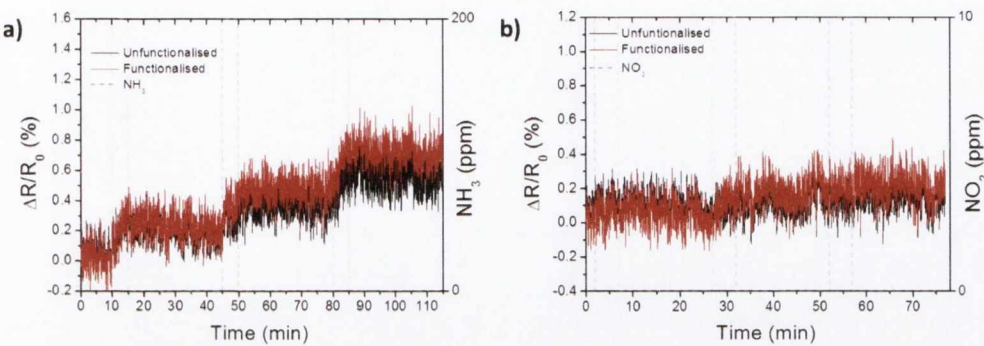


Figure 6.8: Gas sensing response of unfunctionalised and functionalised graphene devices to a) ammonia and b) nitrogen dioxide.

of ammonia, but the SNR is very low. As stated in Section 6.2.2, the SNR must be a least 3 in order to be considered a true gas sensing response.¹⁵⁸ No response to the introduction of 10 ppm of nitrogen dioxide is detected. The lack of response was attributed to the presence of water molecules from the air and also molecule deposition on the surface of the graphene. In order to try and improve performance, the devices were annealed at 70 °C to remove contamination. The graphene remained p-doped after the anneal, as shown in Figure 6.7a and b.

The gas sensing response to ammonia after annealing for both types of device is shown in Figure 6.9a. The response of the device is measured by the ratio of the change in resistance to the original resistance, as shown by Equation 6.2. As ammonia is an n-dopant (electron donor), the resistance of the p-type graphene will increase upon exposure, leading to a positive change in the resistance of the device. Although the change in resistance is larger for the bare graphene, the signal is quite noisy and unstable. In comparison, the functionalised device has less noise and therefore a higher signal-to-noise ratio. The LOD of NH_3 for the functionalised devices is shown in Figure 6.9b. The blue dashed line shows the cut-off of a SNR of 3 and indicates that the

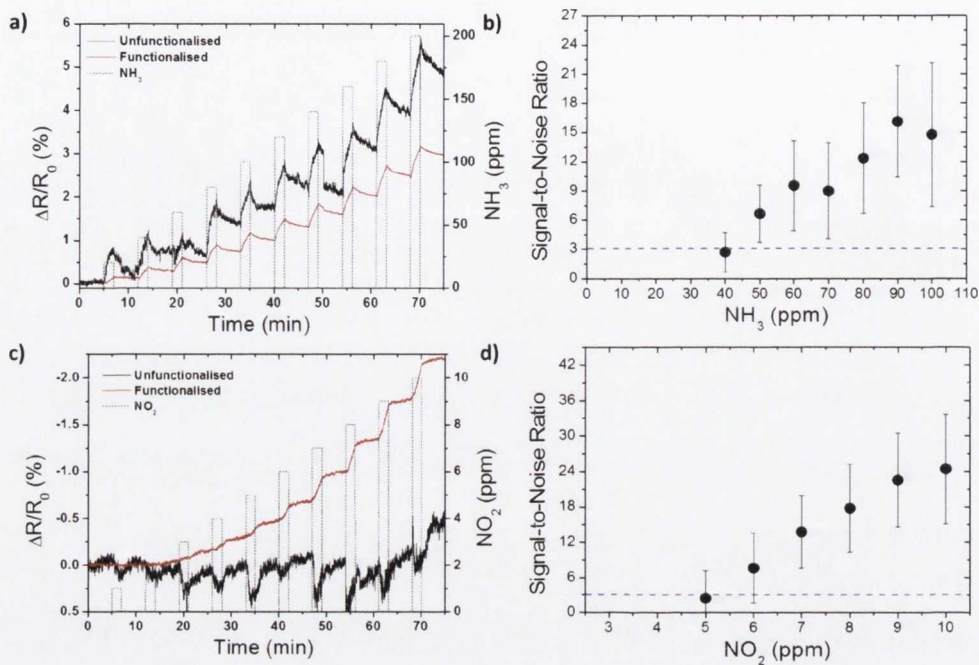


Figure 6.9: a) Gas sensing response of unfunctionalised and functionalised graphene devices to ammonia. b) Limit of detection of ammonia for functionalised device. Blue line indicates SNR of 3. c) Gas sensing response of unfunctionalised and functionalised devices to nitrogen dioxide. d) Limit of detection of nitrogen dioxide for functionalised device.

minimum level of detection is approximately 40 ppm. Similar tests were conducted for NO_2 gas as can be seen in Figure 6.9c and d. NO_2 is a strong p-dopant, therefore the resistance of the p-doped graphene should decrease in its presence. We see this effect by the negative sign of the sensor response upon exposure to NO_2 . In comparison with the functionalised device, the bare graphene shows very little response in the presence of the NO_2 . The LOD for NO_2 is much lower than that for ammonia, at 5 ppm. These results indicate that the functionalised graphene is far more sensitive and reliable as a gas sensor.

FLaT devices

The gas sensing response to NH_3 and NO_2 of a device produced using the FLAT method is shown in Figure 6.10a and c. These devices did not require annealing in order to produce a sensing response, indicating that the presence of the dense molecular layers reduces the amount of contamination to the graphene surface, as observed before in the transfer curves shown in Figure 6.6c. The sign of the resistance change is in agreement with n- and p-type doping from NH_3 and NO_2 , respectively. The limit of detection for both gases is lower than that of the post-transfer functionalised devices, at approximately 20 ppm for NH_3 and 3 ppm for NO_2 , as seen in Figure 6.10b and d. This is in agreement with the observations of Dan *et al.* who observed that

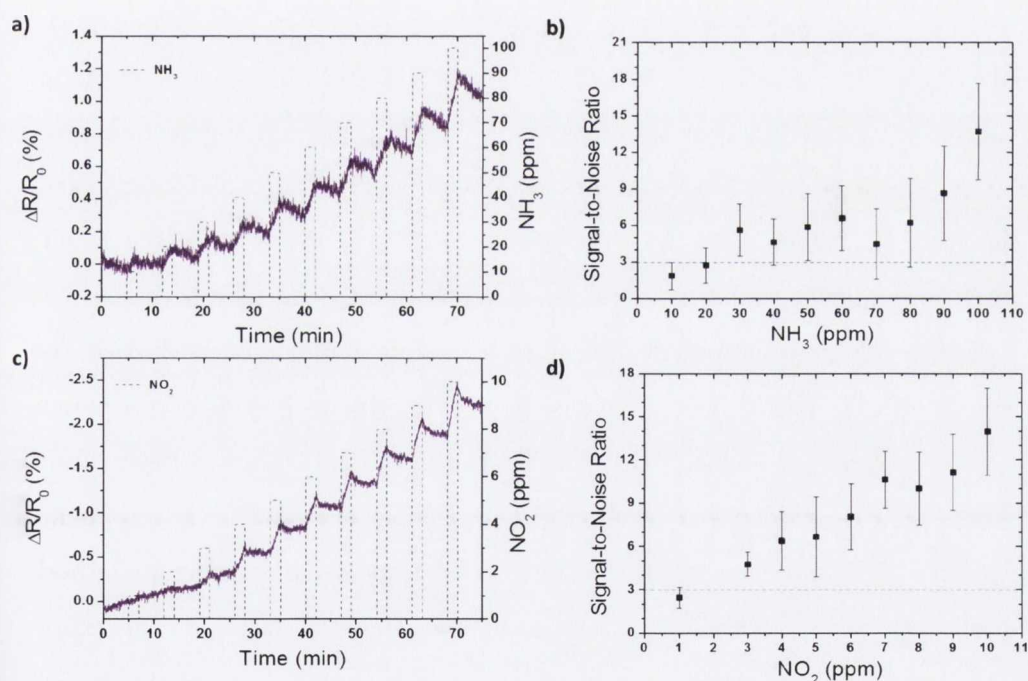


Figure 6.10: a) Gas sensing response and b) limit of detection of FLAT processed graphene device for ammonia. c) Gas sensing response and d) limit of detection of FLAT processed graphene devices for nitrogen dioxide.

the graphene surface must be functionalised to produce a sensing response. This is caused by the trapping of gas molecules within the functionalisation layer. The superior sensor response of the FLaT processed devices is due to the presence of a dense and highly ordered film of **1** and demonstrates the superior quality of molecular films produced using the FLaT method.

6.4 Conclusions

The fabrication of graphene FETs functionalised with **1** has been demonstrated. From analysing the CNP shifts it is evident that the **1** molecules n-dope the graphene. Comparison of FETs that have been produced with graphene functionalised by post-transfer and the FLaT method demonstrate that FLaT produces a graphene film that is encapsulated and thus experiences less contamination. The denser film of **1** results in superior electron mobilities, suggesting that the density of the molecules on the surface produces a homogeneous potential on the surface of the graphene. Large variations in the calculated values for electron and hole mobility in the FLaT processed indicate that contact effects are dominant in these devices.

Gas sensing measurements for both ammonia and nitrogen dioxide reveal that the functionalised graphene devices produce superior performance to that of bare graphene. The FLaT produced FETs have a lower limit of detection in comparison to the devices functionalised after the graphene transfer. This indicates that the FLaT technique is a promising method for the production of functionalised graphene devices as it avoids the exposure of the FETs to water and other solvents which can degrade the device properties and requires them to undergo an annealing cleaning procedure to be utilised in sensing applications. The superior performance of function-

alised devices indicates that the **1** molecules act as a passivation layer on the graphene, which helps to trap gas molecules and increases the SNR and provides stability to the gas sensing response. The denser molecular layer of the FLaT transferred graphene provides more effective passivation and therefore an increased limit of detection of 20 ppm for ammonia and 3 ppm for nitrogen dioxide, in comparison to the 40 ppm and 5 ppm, respectively, of post-transfer functionalised devices. Although the presence of **1** does not induce selectivity in the graphene sensor, the significantly improved limits of detection are promising for the integration of these types of functionalisation agents onto graphene gas sensors.

Chapter 7

Derivatisation of Aromatic Molecules on Graphene

7.1 Introduction

Over recent years, graphene has attracted growing interest as an active material in biological sensors. In order to create selective biosensors based on graphene, it is necessary to immobilise antibodies onto the surface to detect biomarkers for specific diseases. One of the methods of achieving this is to employ an aromatic molecule as an anchor to the graphene and reacting the functional groups of the molecule with the antibody. The most common pathway to link the antibody and the molecule is the reaction of carboxylic acids with amine groups. In this chapter, the feasibility of this reaction using the carboxylic acid groups of **1** was investigated in order to determine if the perylenes will be useful anchor units for graphene-based biosensing applications. The reaction of the carboxylic acid groups of **1** with ethylenediamine (EDA) using O-(7-azabenzotriazole-1-yl)-N,N,N,N-tetramethyluronium hexafluorophosphate (HATU) as the coupling agent, was investigated as proof-of-

concept for the coupling reaction on graphene. The importance of the stability of the molecular layer during the liquid-phase reaction is discussed, along with the implications for utilising aromatic molecules as anchors in graphene-based biosensors. Finally, the ability of the amine-terminated graphene surface to attract *Escherichia coli* (*E. coli*) bacteria is demonstrated.

7.1.1 Molecular stability on graphene

Very few studies of the stability of molecular films on graphene have been undertaken. It is commonly assumed that aromatic molecules remain adhered to the surface during liquid-phase processing due to the strong nature of the π - π interaction between aromatic molecules and graphene. However, Mann *et al.* demonstrated through electrochemical measurements that molecules consisting of a single pyrene base desorbed from CVD graphene in solution, with coverage decreasing by 50% within 8 minutes.¹⁶⁰ In order to prevent this, they designed a molecule with three pyrene "feet" in order to increase interaction with the graphene substrate, resulting in a molecular layer that reduced by only 14% in 12 hours. The structures of the single pyrene and tripodal molecules are shown in Figure 7.1. The functional group placed at the top of the tripod can be altered to suit the application for which the molecule is required. In this case, they attached a Co(II) *bis*-terpyridyl complex in order to utilise the $\text{Co}^{2+/3+}$ redox couple to determine the coverage and stability of the molecular layers electrochemically. Further work by the same group compared the stability of tripods with feet composed of naphthalene, phenanthrene or pyrene, which contain two, three and four aromatic carbon rings, respectively.¹⁶¹ They discovered that the stability of the films increased with the increasing number of rings contained within the tripod feet, suggesting that larger aromatic molecules would form even more stable

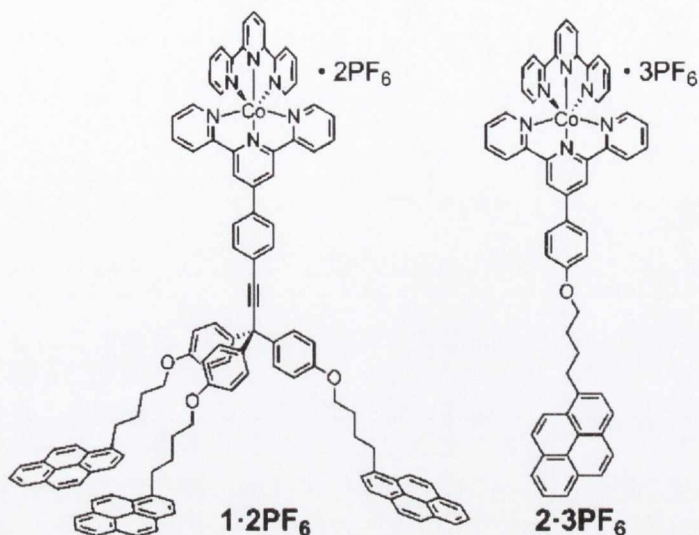


Figure 7.1: Structures of a tripodal molecule with pyrene feet ($1 \cdot 2PF_6$) and a similar molecule ($2 \cdot 3PF_6$) with only one pyrene for binding to a graphene surface. Image obtained from Mann *et al.*¹⁶⁰

films. As a result of this, it is reasonable to expect that perylene derivatives such as **1** are highly stable on graphene due to their larger aromatic core. An alternative method to ensure stability of pyrene on graphene was implemented by Singh *et al.*, who demonstrated electropolymerised pyrene films on graphene for a graphene-based surface plasmon resonance (SPR) sensor.¹¹³

7.1.2 Biofunctionalisation of graphene

The introduction of biological molecules onto graphene is an area of intense research in order to achieve its integration into various biomedical and biosensing applications.^{162,163} This is necessary to ensure selectivity of graphene sensors as antibodies can be added to the surface to bind with indicators (antigens) for specific diseases. This antibody-antigen interaction is typically described as a "lock and key" mechanism as only specific pairs

will bind together. Many studies have focused on the biofunctionalisation of graphene oxide flakes as the presence of carboxylic acid groups on the surface of the flakes can be used to covalently bind biologically relevant molecules to the surface.^{4,162} In addition, liquid-exfoliated flakes that are functionalised with hydrophilic molecules have also been investigated as they can be easily processed in aqueous buffer solution which is compatible with biological molecules.^{4,156}

CVD graphene has also become of interest for biosensing applications as it offers large-area production of high-quality graphene. As CVD graphene does not contain functional groups, it is generally noncovalently functionalised with aromatic molecules on the surface, as depicted in Figure 7.2.^{101,113} The molecules are then used to covalently bind specific antibodies or peptides to the surface in order to selectively detect the analyte. Stability of the anchor molecules during this further functionalisation process is vital for the

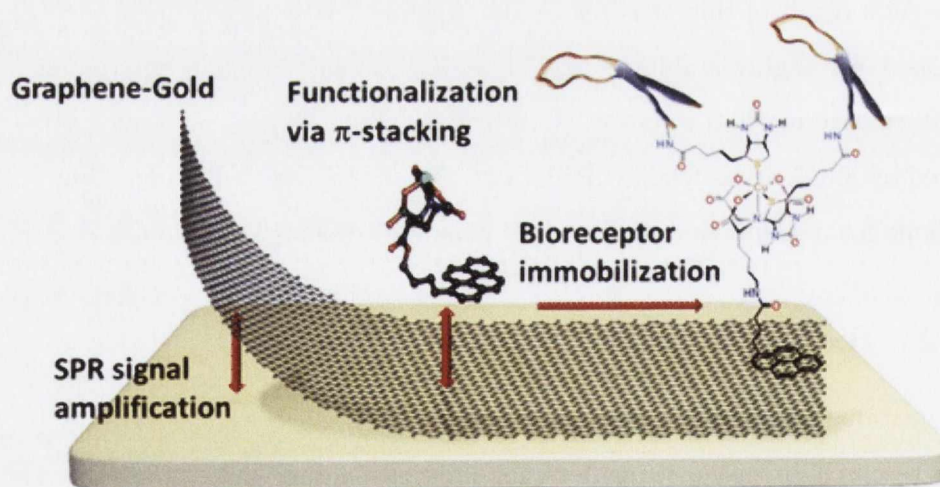


Figure 7.2: Schematic representation of typical graphene biosensor surface. Graphene is functionalised with an aromatic molecule by π - π interactions. The functional groups of the molecule are then used to immobilise bioreceptors for the analyte. This image is adapted from Singh *et al.*¹¹³

development of graphene biosensing devices that must be exposed to solvent or aqueous solutions.¹⁶⁴ A wide variety of molecules have been used, with pyrene-based derivatives being the most popular, despite the concerns over their stability which have been described in Section 7.1.1.

Carboxylic acid to amine coupling

The reaction between carboxylic acids and amines is incredibly important to biochemical coupling as the majority of proteins and antibodies contain both these functional groups.¹⁶⁵ By exploiting this knowledge, it is possible to anchor antibodies to a surface by placing one functional group on the surface and targeting the other for binding. The relevant antibody is then bound to the surface by an amide bond formed between the amine and the carboxylic acid.

One of the most common methods of forming an amide bond between molecules is through the use of a carbodiimide coupling agent such as EDC (1-ethyl-3-(3-dimethylaminopropyl)carbodiimide hydrochloride).¹⁶⁶ EDC reacts with a carboxylic acid group to form an active intermediate which can subsequently react with an amine containing group to form an amide bond. However, the intermediate is easily hydrolysed in aqueous solution, which can reduce the efficiency of amide bond formation. To prevent this hydrolysis, an additional reagent, *N*-hydroxysulfosuccinimide (sulfo-NHS), is typically used in tandem with EDC. The sulfo-NHS reacts with the intermediate formed by EDC and the carboxylic acid group, creating a stable sulfo-NHS intermediate which is not easily hydrolysed. This results in a much greater yield of amide bonds within a solution. The reaction process is pictured in Figure 7.3.

Another method of achieving coupling between a carboxylic acid and an amine group is to use the reagent HATU, which was first published by

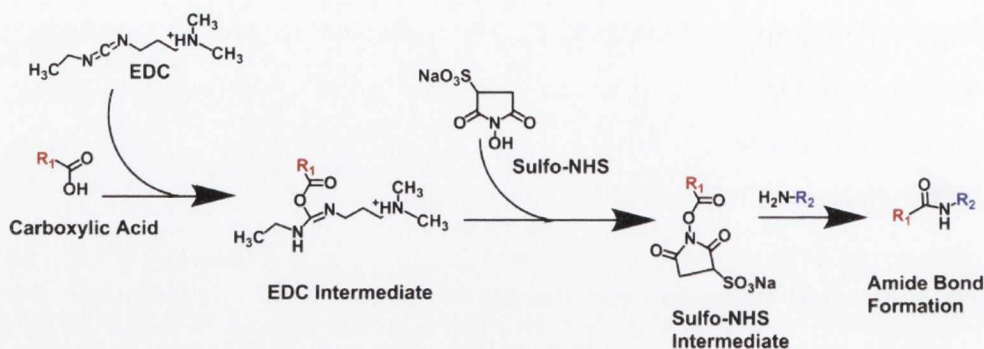


Figure 7.3: Coupling reaction utilising EDC/sulfo-NHS as the cross-linking agents. The efficiency of the reaction is increased by the formation of the sulfo-NHS intermediate, which is more stable in aqueous solution than the EDC-intermediate.

Carpino in 1993.¹⁶⁷ The HATU will react with the carboxylic acid to form an intermediate which subsequently reacts with the amine containing molecule. The mechanism of the reaction is shown in Figure 7.4a. This method was used by Mohanty and Berry to produce an amine-functionalised graphene surface by coupling ethylenediamine (EDA) with the carboxylic acid groups from graphene oxide.¹⁶⁸ Their coupling method was utilised in this thesis in order to convert the carboxylic acid groups of **1** to amine groups as a proof-of-concept experiment to show that **1** can be a useful and versatile platform for producing graphene surfaces that are compatible with biological systems. This reaction would form an amide link between **1** and one of the amine groups of EDA, leaving the second amine of EDA as the end functional group, as depicted in Figure 7.4b.

7.1.3 Bacterial attachment to graphene

In addition to molecular sensing applications, graphene is also of interest for detection of the presence of bacteria. One of the first bacterial sensors was produced by Mohanty and Berry, where they demonstrated detection

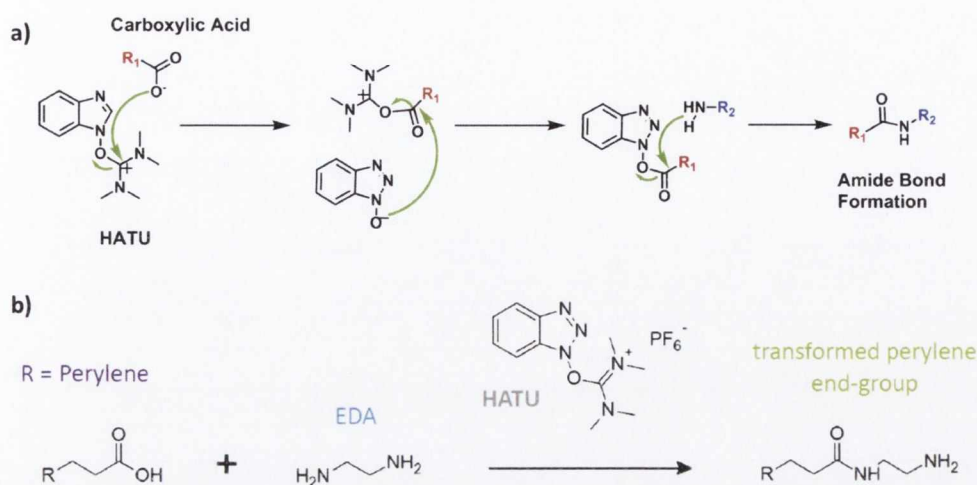


Figure 7.4: a) Reaction mechanism for coupling of carboxylic acids to amines utilising HATU as the cross-linking agent.

of a single cell of *Bacillus cereus* using a film of amine-terminated graphene flakes.¹⁶⁸ The outer cell wall of bacteria typically carries a negative charge due to the presence of lipopolysaccharides in the membrane (Figure 7.5).^{169,170} As a result of this, it is possible to attract bacteria to a surface *via* Coulombic interactions by introducing a positive charge to the surface. Amine groups can be used for this as they are positively charged by the addition of a proton in buffer solution at physiological pH (pH 7.4).^{165,168}

Further work in this area used antibodies in order to ensure selective adhesion of specific bacterial species to the graphene surface. Huang *et al.* used pyrene molecules containing an N-hydroxysuccinimide ester to anchor anti-*E. coli* antibodies to a CVD graphene transistor.¹⁷¹ The sensor responded to the initial presence of the bacteria and also to the alteration of pH of the surrounding environment due to the metabolism of glucose by the bacteria on the surface. Mann *et al.* demonstrated that their pyrene tripod molecules, described in Section 7.1.1, could be used to increase *E. coli* adhesion on CVD

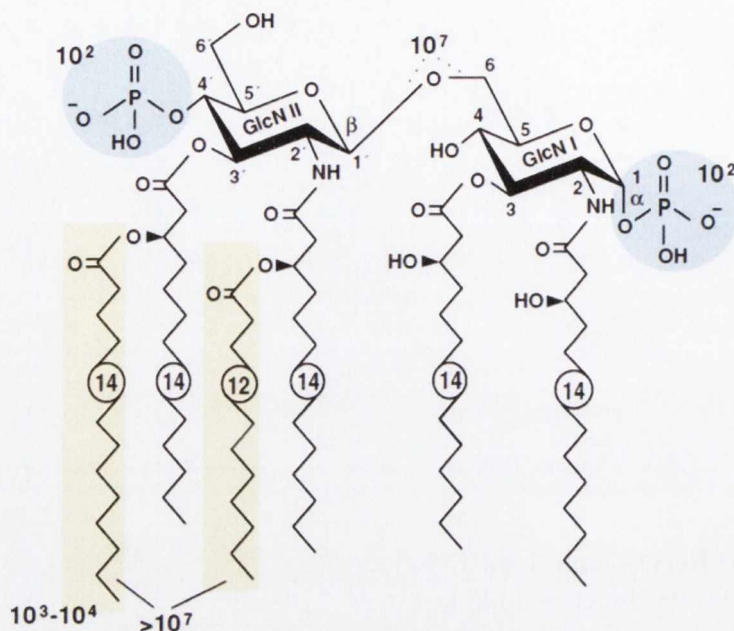


Figure 7.5: Structure of lipopolysaccharide molecule. The negatively charged phosphate groups are highlighted in blue. Image obtained from Alexander and Rietschel.¹⁷⁰

graphene by controlling the orientation of the antibody molecules to ensure better interaction between the bacteria and the antibody.¹⁷²

7.2 Experimental Details

1 was deposited onto CVD graphene via the two methods outlined in Chapter 5, *i.e.* dropcast onto graphene that had already been transferred to SiO₂ or using the FLaT method. The substrates were then immersed in 25 ml of EDA containing 5 mg of HATU for 6 hours in order to initiate a coupling reaction between EDA and the carboxylic acid groups of **1**.¹⁶⁸ The functionalisation was investigated using Raman and X-ray photoelectron spectroscopy.

Bacterial adhesion tests were conducted in order to further confirm the

presence of amine groups on the graphene surface. These tests were undertaken in collaboration with Dr. Rohit Mishra in the laboratory of Prof. Martin Hegner in CRANN. To produce a bacterial solution, *E. coli* bacteria were cultured in lysogeny broth (a standard bacterial growth medium) at 37°C. A PDMS fluid cell was designed to bring the graphene surface in contact with the bacteria under incubation conditions to avoid sample drying and maintain a favourable environment for the bacteria. The production of the fluid cell is detailed in Section 3.1.6. The fluid cell is depicted in Figure 7.6; a purple dye was used in this picture to ensure ease of visualisation.

After 20 minute incubation, the sample was subsequently rinsed with 0.85% NaCl solution to remove the lysogeny broth, which can interfere with fluorescence measurements by binding with the fluorescent dye. The PDMS cell was then removed to enable the bacteria to be stained for fluorescence imaging. Details of the fluorescence micro-

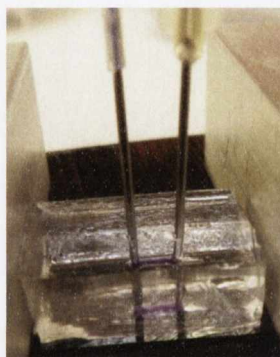


Figure 7.6: PDMS fluid cell.

scope are provided in Section 3.2.8. Propidium iodide fluorescent dye was applied to the bacteria and incubated for 15 minutes. A cover slip was then placed over the sample to obtain fluorescence images. The image area was 23,364 μm^2 . The average density of bacteria on each sample was calculated by counting the number of bacterial cells in each image and dividing by the area. A histogram was constructed using this data, error bars indicate the standard deviation.

7.3 Results and Discussion

7.3.1 Stability of aromatic molecules on graphene

After initiating the coupling reaction, significant differences depending on the original packing density of the perylene molecules were observed. These differences can be seen in the Raman maps presented in Figure 7.7. For low density samples the molecules are mostly removed during the coupling process and are only present in aggregates on the surface (Figure 7.7a). The corresponding Raman spectra for both aggregate and bare graphene areas in the low density sample are shown in Figure 7.7b.

In the case of the more ordered high density samples, the molecules are still present in a uniform film after the functionalisation process, as can be observed in the Raman map of the **1** peaks (Figure 7.7c). By comparing the average Raman spectra (Figure 7.7d), it is observed that after functionalisation the intensity ratio of **1**:G decreases from 1.3 to 1.1, indicating that the packing density of the molecules has been decreased. This can most likely be attributed to the increase in carbon chain length upon addition of the ethylenediamine, which forces the molecules to rearrange in order to accommodate the more sterically demanding end-chains. It was observed in Chapter 5 that the higher packing density samples exhibited a more stable and uniform film, with stronger molecule-molecule interactions than the lower density samples. The removal of molecules during functionalisation of low packing density samples clearly demonstrates that the formation of ordered films exploiting molecule-molecule interactions is a prerequisite for further derivatisation. This is an important result with regard to understanding the behaviour of molecules during functionalisation on graphene, as

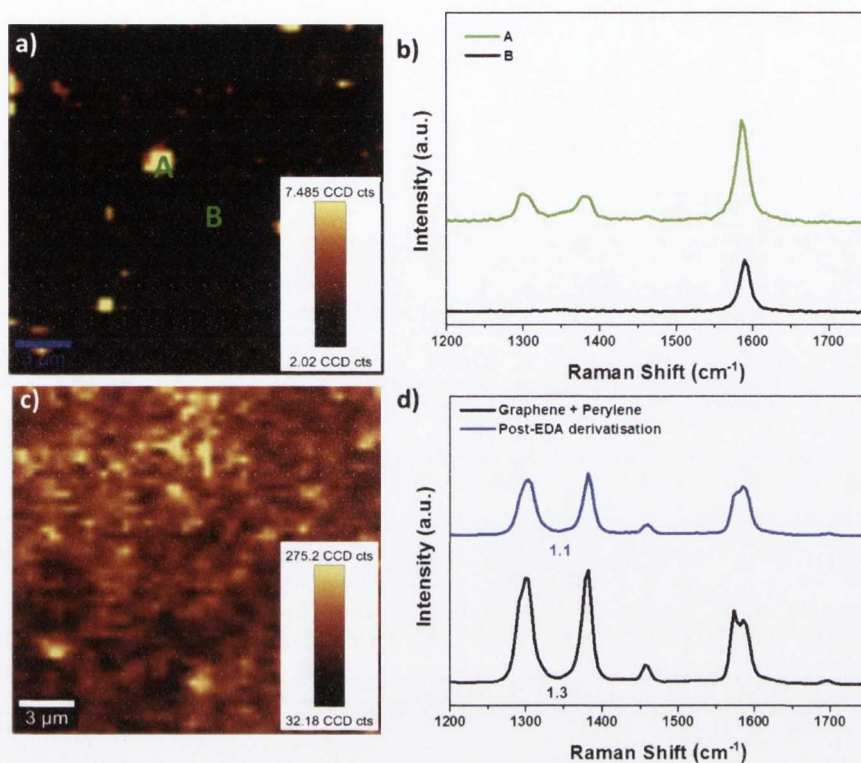


Figure 7.7: (a) Raman map of **1** peak intensity after derivatisation of low density sample. (b) Corresponding Raman spectra of areas A and B in map. (c) Raman map of **1** peak after derivatisation of FLaT sample. (d) Raman spectra of **1** deposited on graphene by FLaT before (black) and after amine-derivatisation (blue).

it is generally assumed that aromatic molecules will adhere strongly to the graphene surface due to π - π stacking. In this case it can be seen that even with a large aromatic core, **1** can still be removed unless in a densely packed configuration which allows intermolecular forces to stabilise the film.

7.3.2 X-ray Photoelectron Spectroscopy

While the decrease in packing density observed by Raman spectroscopy indicates an increase in the chain length of the end-groups of **1**, it may also be

indicative of a partial desorption of molecules on a smaller scale than that observed in low packing density samples. Therefore, in order to verify the success of the reaction, the chemical species present after derivatisation must be identified. For this reason, XPS was employed to confirm the success of the EDA-derivatisation on high packing density films. Survey scans of **1** on graphene before and after derivatisation are shown in Figure 7.8a. The C 1s and O 1s peaks are clearly visible, along with the Si 2s and 2p peaks from the substrate. The N 1s peak intensity is too low in comparison to the C

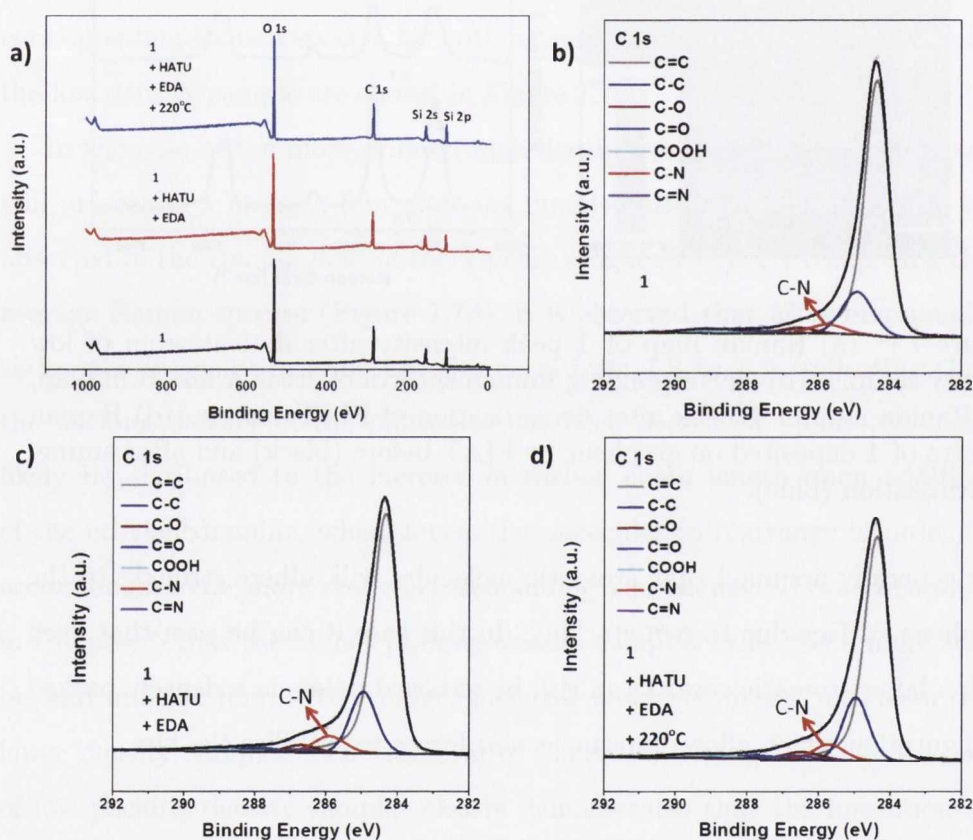


Figure 7.8: (a) XPS survey scans and (b-d) high resolution C 1s spectra of **1** on graphene before and after EDA derivatisation and a 220 °C anneal. The C-N contribution has increased after derivatisation.

1s and O 1s peaks to be seen in the surveys. This can be attributed to two factors: the percentage of nitrogen present is very low in comparison to the other elements and in addition, the N 1s peak has a lower absorption cross section, resulting in a lower signal. However, when repeatedly scanning the area of the N 1s peak a clear signal can be obtained as shown in Figure 7.9. High resolution C 1s spectra are shown alongside the survey scans. The peak is dominated by the asymmetric component that corresponds to sp^2 carbon from the graphene and perylene cores. There is a smaller component which corresponds to sp^3 carbon which can be attributed to the dendritic chains of the perylene. After derivatisation, there is an increase in the C-N bond contribution, as seen in Figure 7.8c and d, indicating the presence of amide and amine bonds. This contribution remains after a 220 °C anneal, indicating that the derivatisation was successful.

For further information on the exact nature of the nitrogen containing species, high resolution spectra of the N 1s core-level of the various samples were obtained. The initial spectrum of **1** as deposited on graphene is shown in Figure 7.9a. It can be deconvoluted into two contributions, originating from the two different nitrogen environments in the molecule (imide and amide, inset). The areas of each peak are roughly equal, with the broader amide component indicating slightly higher disorder in the dendritic tails than in the perylene core. After the reaction with EDA, the deconvolution of the N 1s spectrum shows two additional nitrogen components and there is an increase in the imide and amide contributions (Figure 7.9b), which is attributed to the creation of amide linkages and the addition of terminating amine groups. The two additional peaks are assigned to the presence of HATU and side product residues as the coupling agent contains additional nitrogen species (inset, Figure 7.9b).

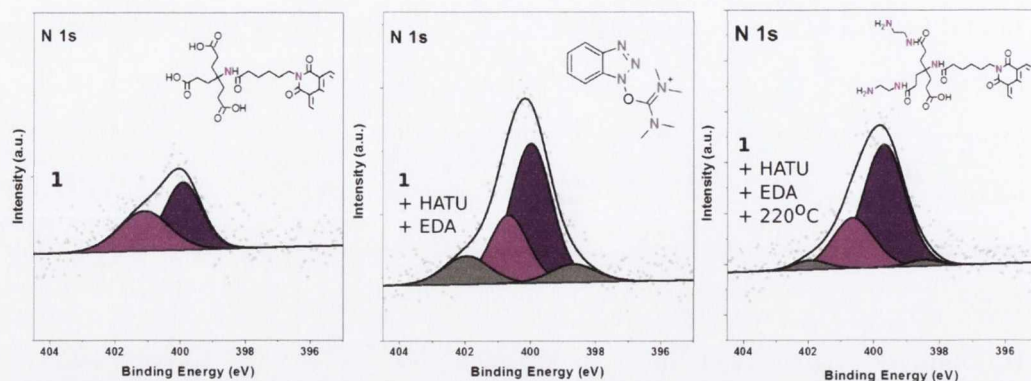


Figure 7.9: Evolution of XPS spectra of perylene on graphene. (a) As-transferred **1** on graphene. Inset: Partial structure of **1** with corresponding nitrogen contributions. (b) **1** on graphene after reaction with HATU and EDA. The two new contributions are from HATU residue. Inset: Chemical structure of HATU. (c) After 220 °C anneal of derivatised sample. The HATU contributions have been reduced, but the amine signal is still increased. Inset: Partial structure of **1** after reaction, depicting corresponding nitrogen contributions.

In order to eliminate the possibility of adsorption leading to the changed XPS spectrum, annealing was employed in order to desorb the small reactants from the surface. An anneal at 220 °C results in a decrease in the HATU contribution, as seen in Figure 7.9c. The increased amine is still present after annealing, and appears to be larger than the amide component after the annealing step, which is surprising since a complete transformation of the carboxylic acid end-groups to amide bridges leading to amine end groups would have equal amounts of amines and amides. The increase can also not be attributed to physisorbed EDA as the small molecule would most likely have desorbed during the anneal. However, the deconvolution and extraction of relative intensities of the components are comparatively inaccurate in this case due to the high FWHM of the peaks and the number of different nitrogen containing compounds involved in the reaction. Despite this inaccuracy, the

overall significantly increased intensity of amine and amide components after annealing indicates that the ethylenediamine has successfully coupled with the carboxylic acid groups on the **1** molecule. Due to the perpendicular orientation of the molecules on the graphene, as seen in Chapter 5, full coupling is not expected to occur as at least one carboxylic acid group will be obscured by the presence of those above.

7.3.3 Bacterial adhesion to graphene

In order to further verify the presence of amine end-groups on the graphene surface and demonstrate the viability of this functionalisation method for biological applications, the adhesion of bacteria was tested using fluorescence microscopy. *E. coli* are gram-negative bacteria, with a negatively charged cell wall, which are attracted to positively charged amine groups due to electrostatic interaction, as described in Section 7.1.3. Fluorescence images of *E. coli* bacteria on bare graphene and graphene with **1** before and after derivatisation are presented in Figure 7.10, along with a histogram indicating the average number of bacteria present on each sample. On bare graphene and graphene with **1** (Figure 7.10a and b), only a few bacteria are present. The bare graphene and graphene with **1** contain $0.9 (\pm 0.5) \cdot 10^4$ bacteria cm^{-2} and $2.6 (\pm 0.9) \cdot 10^4$ bacteria cm^{-2} , respectively. This is attributed to non-specific adsorption as the bare graphene surface contains no charge to attract the bacteria.¹⁷² When graphene is functionalised with **1**, the surface may contain some negative charge due to deprotonated carboxylic acid groups which would repel the negatively charged bacteria. In contrast, the amine-modified **1** surface (Figure 7.10) contains $11.7 (\pm 4.8)$ bacteria $\cdot 10^4 \text{ cm}^{-1}$, which is an order of magnitude increase in the density of bacteria present on the surface, indicating increased interactions between the graphene and the bacteria due

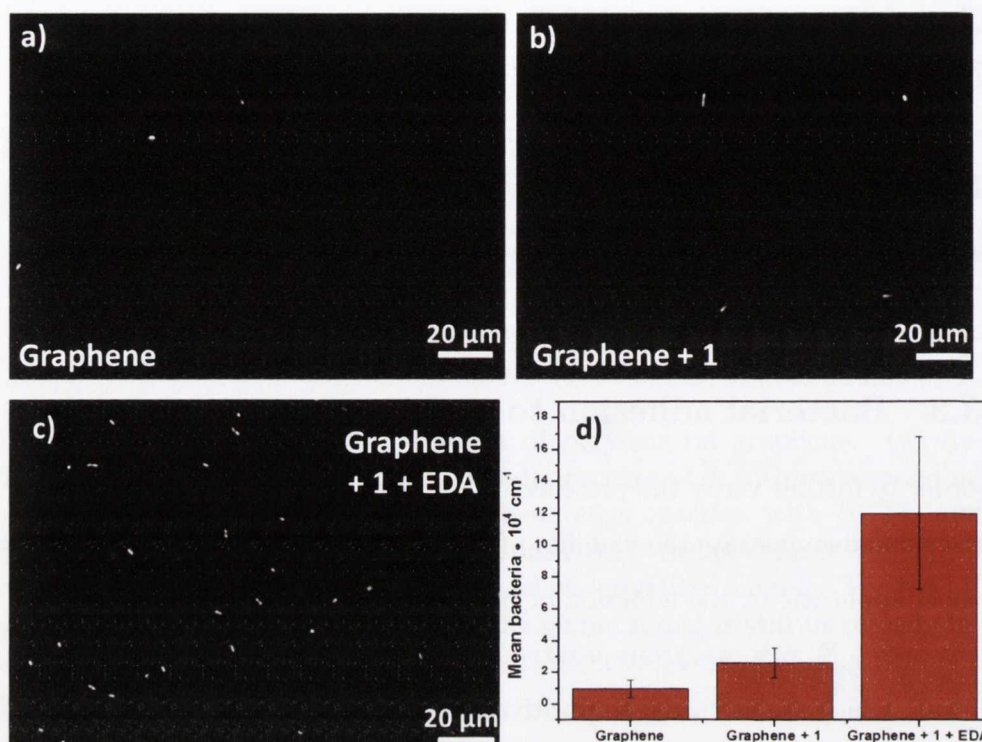


Figure 7.10: Fluorescence images of *E. coli* bacteria on (a) graphene (b) **1** on graphene and (c) **1** on graphene after amine-functionalisation. Scale bars are 20 μm. (d) Histogram indicating the average number of bacteria in each image.

to the presence of amine groups. The average number of bacteria present on the different surfaces is summarised in the histogram in Figure 7.10d. This ability of the derivatised graphene surface to immobilise bacteria from a solution has potential to be harnessed to detect bacteria using optical, mechanical or electrical sensors.

7.4 Conclusions

In this chapter, the derivatisation of films of **1** has been investigated in order to determine their suitability for future biosensing applications. The

significantly increased stability of the high packing density films produced using FLaT has been demonstrated during an on-surface derivatisation process. For low packing density **1** films, the molecules are removed during a biochemical coupling reaction, while the high packing density film remains stable. This observation is vital to the integration of graphene into biosensors as their selectivity hinges upon the ability of the aromatic molecules to anchor selective antibodies to the graphene surface. Therefore the packing density and stability of any potential aromatic anchor must be assessed before use in a biosensor. The alteration of the functional end-groups of **1** from carboxylic acid to amine has been characterised by Raman spectroscopy and XPS. In addition, fluorescence images demonstrate increased adhesion of *E. coli* bacteria to the amine-functionalised graphene. This opens the path to the integration of these films into graphene-based bacterial sensing devices.

Chapter 8

Conclusions and Future Work

This thesis presents the alteration of graphene in two ways: the production of folds and structures of graphene and the introduction of surface functionalities *via* non-covalent functionalisation.

The formation of 3D structures of graphene was achieved by integrating a printing step into the standard CVD graphene polymer-assisted transfer process. Upon removal of the copper growth substrate, the graphene was placed upon a PDMS stamp patterned with trenches. SEM analysis of the conformation of the graphene on the stamps revealed that increasing the trench depth of the stamps led to increased tearing of the graphene sheet in order to relieve strain while drying onto the stamp surface. The final 3D printed structures of graphene conform to the PMMA scaffold, as observed using SEM and AFM. Raman spectroscopic analysis was used to differentiate between the effects of strain and doping in the graphene due to contact with the polymer scaffold. It was concluded that strain is released while the graphene is on the PDMS stamps and therefore the shifts in the Raman peak positions are due to doping from the polymer substrate. The increase in surface area due to the folding of the graphene is demonstrated through

electrochemical measurements in background electrolyte. Although these structures do not produce strained graphene, the increased surface area may still be useful in device applications such as sensors or as electrodes in solar cells. The trenched structure also results in the formation of channels of graphene, which may be integrated into microfluidic setups.

The remainder of the thesis focuses on the functionalisation of graphene with a perylene bisimide derivative. Raman spectroscopy revealed that the packing density of the molecules is dependent upon the cleanliness of the graphene substrate. Higher packing density films were produced when the graphene had been annealed in order to remove PMMA residue. STM revealed that these highly packed films formed a stable, ordered monolayer on the graphene. It was also observed that the molecules adsorb perpendicular to the graphene surface, which is contrary to other studies which have demonstrated a planar conformation for molecules containing a large aromatic core. Fluorescence measurements indicate that the lower packed films also contain areas of perpendicularly orientated molecules. This observation reveals that the formation of molecular layers on graphene is governed by a variety of intermolecular and surface forces which must be considered when choosing the deposition method for a molecule on graphene.

An alternative method of producing functionalised graphene, termed functional layer transfer (FLaT), was also developed. This process streamlined the production of high density molecular films on graphene and led to improved gas-sensing performance in functionalised graphene field effect transistors, in comparison with low packing density films. The higher packed films were also more stable during an on-surface derivatisation process where the carboxylic acid groups of the perylene were converted into amine groups.

Future work should explore the introduction of other molecules to graphene

through FLaT as a versatile means of tailoring the surface functionality of a graphene sheet. In addition, extension of the derivatisation process to include specific antibodies or peptides is essential for the development of a specific graphene biosensor.

Some preliminary work towards creating a biosensor using a graphene-silicon Schottky diode has been undertaken. Previously, sensing of solvents using this device has been demonstrated, as shown in Figure 8.1.¹⁷³ In addition to the change in current levels, parameters such as the diodes ideality factor, η , sheet resistance, R_S , and Schottky barrier height, ϕ_B , varied upon exposure to different solvents. These sensors exhibited full recovery and were incredibly robust and stable over a period of 30 days. Due to these properties, their potential for sensing of *E. coli* bacteria in aqueous solution was investigated.

The surface of a graphene-Si Schottky diode was functionalised with the perylene bisimide derivative and subsequently amine-derivatised following the same procedure outlined in Chapter 7. The PDMS cell featured in the same chapter was placed over the diode surface, as shown in Figure 8.2a. The

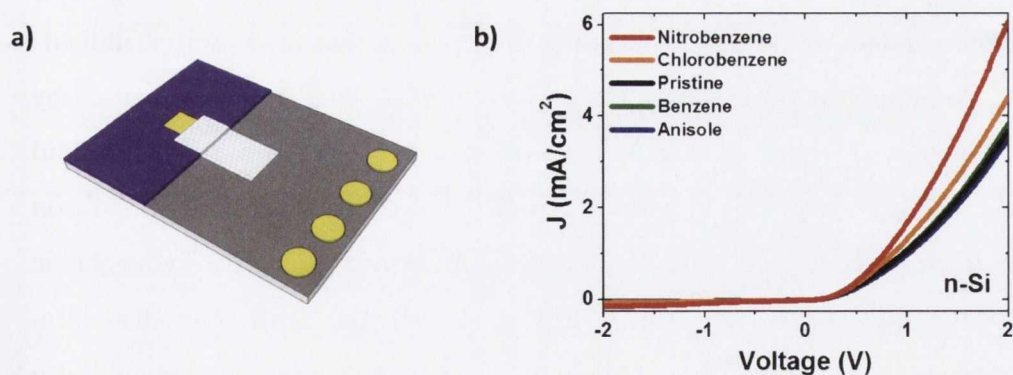


Figure 8.1: a) Schematic of Graphene-Si Schottky diode. b) Diode response upon exposure to various solvents.

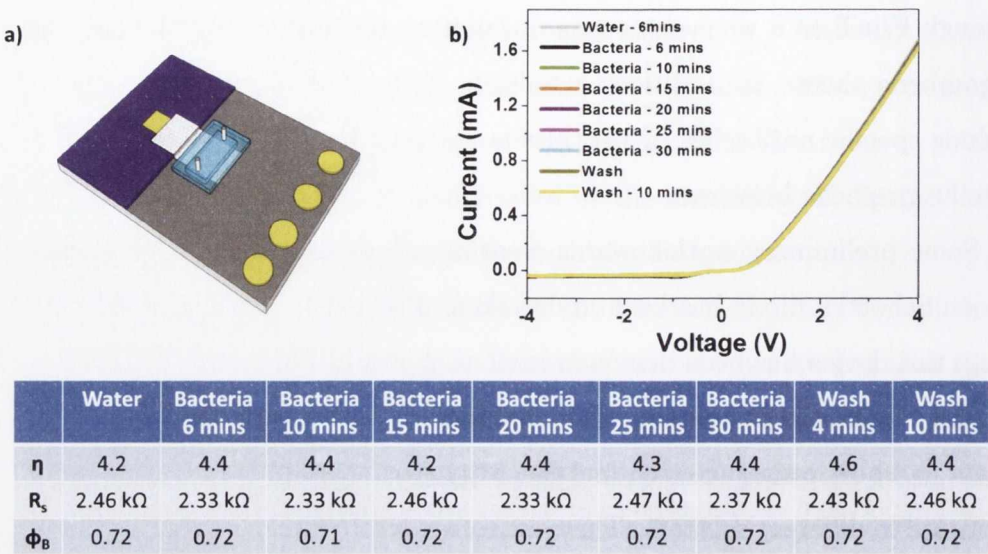


Figure 8.2: Upper: a) Schematic of Graphene-Si Schottky diode integrated with a PDMS fluid cell. b) Diode response upon exposure to water and *E.coli*. A new measurement was taken at each time point. Lower: Table of variation of diode parameters over time after exposure to bacteria.

response of the diode to water and the presence of bacteria was recorded. The diode curve exhibits no significant change over the course of the measurement sequence. In addition, the diode parameters show fluctuations, but no discernible pattern can be observed. Other measurement sequences demonstrated an increase in sheet resistance after exposure to water, indicating a degradation of the graphene-silicon interface, which may be caused by oxidation of the silicon to SiO_2 . In order to achieve integration with a fluid cell for these diode devices, the interface between the graphene and silicon must be protected from this oxidation by implementation of a hydrophobic SAM. GFET devices may offer an alternative to the diodes and their integration with the fluid cell and compatibly with aqueous solution should also be investigated.

To conclude, there has been much interest in utilising graphene for a

variety of applications. However, in order to achieve this goal, the mass production and processing of graphene must be optimised. CVD of graphene and its subsequent transfer are currently the most promising methods to provide large-scale graphene films. This thesis presents the ability to manipulate graphene's properties by modifying the transfer process using two methods. The integration of a printing step has resulted in the production of folded graphene structures and the development of FLaT provides a high-throughput method for producing non-covalently functionalised graphene. These processes provide a means to alter graphene's surface area and chemical properties with very little interference to the standard transfer, which is an essential step towards the optimisation of graphene processing.

Publications and Presentations

Publications

1. "Production of 3D-shaped graphene *via* transfer printing"

Sinéad Winters, Toby Hallam, Hugo Nolan, Georg S. Duesberg, *physica status solidi b*, **249** (12), 2515-2518 (2012)

2. "Investigation of carbon-silicon schottky diodes and their use as chemical sensors"

Georg S. Duesberg, Hye-Young Kim, Kangho Lee, Niall McEvoy, **Sinéad Winters**, Chanyoung Yim, *Proceedings of the European Solid-State Device Research Conference (ESSDERC)*, 85-90 (2013)

3. "Investigation of the optical properties of MoS₂ thin films using spectroscopic ellipsometry"

Chanyoung Yim, Maria O'Brien, Niall McEvoy, **Sinéad Winters**, Inam Mirza, James G. Lunney, Georg S. Duesberg, *Applied Physics Letters* **104** (10), 103114 (2014)

4. "Controlled synthesis of transition metal dichalcogenide thin films for electronic applications"

Riley Gatensby, Niall McEvoy, Kangho Lee, Toby Hallam, Nina C

- Berner, Ehsan Rezvani, **Sinéad Winters**, Maria O'Brien, Georg S. Duesberg, *Applied Surface Science* **297**, 139-146, (2014)
5. "Noncovalently Functionalized Monolayer Graphene for Sensitivity Enhancement of Surface Plasmon Resonance Immunosensors"
- Meenakshi Singh, Michael Holzinger, Maryam Tabrizian, **Sinéad Winters**, Nina C. Berner, Serge Cosnier, Georg S. Duesberg, *Journal of the American Chemical Society* **137** (8), 2800-2803 (2015)
6. "Preparation of gallium sulfide nanosheets by liquid exfoliation and their application as hydrogen evolution catalysts"
- Andrew Harvey, Claudia Backes, Zahra Gholamvand, Damien Hanlon, David McAteer, Hannah C. Nerl, Eva McGuire, Andres Seral-Ascaso, Quentin M. Ramasse, Niall McEvoy, **Sinéad Winters**, Nina C. Berner, David McCloskey, John F. Donegan, Georg S. Duesberg, Valeria Nicolosi, Jonathan N. Coleman, *Chemistry of Materials* **27** (9), 3483-3493 (2015)
7. "Direct Observation of Degenerate Two-Photon Absorption and Its Saturation of WS₂ and MoS₂ Monolayer and Few-Layer Films"
- Saifeng Zhang, Ningning Dong, Niall McEvoy, Maria O'Brien, **Sinéad Winters**, Nina C. Berner, Chanyoung Yim, Yuanxin Li, Xiaoyan Zhang, Zhanghai Chen, Long Zhang, Georg S. Duesberg, Jun Wang, *ACS Nano* **9** (7), 7142-7150 (2015)
8. "Understanding and optimising the packing density of perylene bisimide layers on CVD-grown graphene"
- Nina C. Berner, **Sinéad Winters**, Claudia Backes, Chanyoung Yim, Kim C. Dömbgen, Izabela Kaminska, Sebastian Mackowski, Attilio A.

Cafolla, Andreas Hirsch, Georg S. Duesberg, *Nanoscale*, **7**, 16337-16342 (2015)

9. "On-surface derivatisation of aromatic molecules on graphene: The importance of packing density"

Sinéad Winters, Nina C. Berner, Rohit Mishra, Kim C. Dömbgen, Claudia Backes, Martin Hegner, Andreas Hirsch, Georg S. Duesberg, *Chemical Communications*, **51**, 16778-16781 (2015)

Oral Presentations

- "Graphene-silicon Schottky diodes for sensor applications." From Solid State to BioPhysics VII, Dubrovnik, Croatia 2014 (Invited Talk)
- "Functionalization of aromatic molecules on graphene for sensor applications." International Conference on Diamond and Carbon Materials, Madrid, Spain 2014
- "Functionalization of Aromatic Molecules on Graphene." MRS Spring Meeting, San Francisco, USA, 2015

Poster Presentations

- "Production of three-dimensional graphene structures *via* transfer printing." IWEPM, Kirchberg, Austria, 2012
- "Production of 3D-shaped graphene *via* transfer printing." Graphene 2013, Bilbao, Spain, 2013
- "Production of 3D-shaped graphene *via* transfer printing." EuroNanoForum, Dublin, Ireland, 2013

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