

PRODUCTION OF GRAPHENE FOR THE FABRICATION OF GRAPHENE FIBRES

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Abstract

Graphene consists of a single atomic layer of carbon atoms arranged in a hexagonal lattice and exhibits two-dimensional properties. This material is of particular interest as it is a highly efficient conductor of heat and electricity and possesses an exceptionally high strength-to-weight ratio. The uses of graphene extend to a variety of industries, including the fields of life sciences; electronics; and chemistry. The properties of graphene are largely determined by the method of fabrication thereof. These methods include chemical vapour deposition as well as mechanical and chemical exfoliation. In this study, research has been conducted to investigate these various fabrication routes so as to determine a reliable method of producing graphene of a high quality for the production and study of graphene fibres. Specifically, graphene produced via the chemical oxidation of graphite was investigated due to its cost-effectiveness, viability and scalable nature. This process resulted in the production of an intermediate product, graphene oxide, which was then reduced to form graphene. Thermal and chemical reduction methods of graphene were also investigated. The produced graphene exhibits high correlation with graphene reported in the literature. The quality of the synthesised material was analysed using various diagnostic tools, including Scanning and Transmission Electron Microscopy, Energy-Dispersive X-Ray Spectroscopy and X-Ray Diffraction. The graphene was used for the fabrication of graphene fibres with the addition of the polymer materials, polyvinyl alcohol and polystyrene. A microscopic fibre fabrication route was explored and the outcome of this research was the production of graphene nanofibres which may be used in various applications, including strengthening fillers in composite materials.

i. List of Symbols

Greek Letters

μ	Carrier mobility ($\text{cm}^2 \cdot \text{V}^{-1} \cdot \text{s}^{-1}$)
ρ	2D resistivity (Ω)
ρ_{xx}	Longitudinal resistivity ($\text{k}\Omega$)
σ	Conductance ($\text{S} \cdot \text{m}^{-1}$)
σ_{xy}	Hall conductivity ($4e^2 \cdot \text{h}^{-1}$)

Roman Letters

e	Electron charge ($1.602 \times 10^{-19} \text{ C}$)
E	Energy (eV)
E_y	Young's modulus ($\text{N} \cdot \text{m}^{-1}$)
h	Planck's constant ($6.626 \times 10^{-34} \text{ J} \cdot \text{s}$)
k_x	Wave number in the x-direction
k_y	Wave number in the y-direction
n	Charge carrier concentration (cm^{-2})
R_H	Hall resistivity ($\text{k}\Omega \cdot \text{T}^{-1}$)
V_g	Gate voltage (V)

ii. Acronyms

1D	One-dimensional
2D	Two-dimensional
3D	Three-dimensional
AA	Ascorbic acid
AC	Alternating current
AFM	Atomic Force Microscopy
C	Carbon
Cl	Chlorine
CVD	Chemical Vapour Deposition
DC	Direct Current
DMF	Dimethylformamide
EDX	Energy-Dispersive X-Ray Spectroscopy
FEG-SEM	Field-Emission Gun Scanning Electron Microscopy
FTIR	Fourier-Transform Infrared Spectroscopy
G	Graphene
GO	Graphene oxide
GO-1	Graphene oxide from the Hummers' method
GO-2	Graphene oxide from the modified Hummers' method with extended oxidation time
GO-3	Graphene oxide from the modified Hummers' method with additional potassium permanganate
GO-4	Graphene oxide from the Tour method
GO-5	Graphene oxide from the Huang method
H ₂ O ₂	Hydrogen peroxide
H ₂ SO ₄	Sulphuric acid
H ₃ PO ₄	Phosphoric acid
HCl	Hydrochloric acid
HRTEM	High Resolution Transmission Electron Microscope

HV	High Voltage
KMnO ₄	Potassium permanganate
Mn ₂ O ₇	Diamanganese heptoxide
NaBH ₄	Sodium borohydride
NaNO ₃	Sodium nitrate
O	Oxygen
PVA	Polyvinyl alcohol
S	Sulphur
SEM	Scanning Electron Microscope
SiO ₂	Silicon dioxide
TEM	Transmission Electron Microscope
THF	Tetrahydrofuran
XRD	X-Ray Diffraction

Table of Contents

Chapter 1	Introduction.....	1
Chapter 2	Aims and objectives	4
Chapter 3	Graphene and its applications	5
3.1.	Discovery and brief history	5
3.2.	Properties.....	6
3.2.1.	Physical structure	6
3.2.2.	Electronic structure and properties	7
3.2.3.	Conductivity.....	11
3.2.4.	Mechanical properties	13
3.2.5.	Other properties.....	14
3.3.	Synthesis of graphene.....	15
3.3.1.	Synthesis of graphene via chemical exfoliation.....	17
3.3.2.	Synthesis of graphene via ultrasonic exfoliation.....	19
3.4.	Methods of characterising graphene	19
3.5.	Degradation of graphene and graphene oxide	30
3.6.	Applications.....	32
3.7.	Summary	39
Chapter 4	Electrospinning	40
4.1.	The electrospinning process	40
4.2.	The electrospinning apparatus	42
4.3.	Polymers used for electrospinning	43
4.1.1.	Polyvinyl alcohol (PVA)	43
4.1.2.	Polystyrene	43

4.4.	Electrospinning solution parameters	44
4.5.	Electrospinning processing parameters	45
4.5.1.	Delivery system.....	45
4.5.2.	Flow rate.....	46
4.5.3.	Collection system	47
4.5.4.	Tip-to-collector distance	48
4.5.5.	Applied voltage.....	48
4.6.	Ambient parameters	49
4.7.	Characterization of electrospun fibres.....	50
4.8.	Applications of electrospun graphene/PVA composite fibres	52
4.9.	Summary	53
Chapter 5	Synthesis of graphene	54
5.1.	Experimental methods.....	55
5.1.1.	Hummers' method.....	55
5.1.2.	Modified Hummers' method with extended oxidation time	56
5.1.3.	Modified Hummers' method with additional potassium permanganate	57
5.1.4.	Tour method.....	58
5.1.5.	Huang method.....	58
5.2.	Method of washing of graphene oxide	60
5.3.	Observations	60
5.4.	Methods of reducing graphene oxide	67
5.4.1.	Reduction by sodium borohydride	68
5.4.2.	Reduction via ascorbic acid	69
5.4.3.	Reduction via thermal treatment	70
5.5.	Qualitative analysis of synthesised graphene oxide	72
5.6.	Summary	73
Chapter 6	Fabrication of graphene fibres	75
6.1.	The electrospinning apparatus	75
6.2.	The high voltage DC power supply.....	78

6.3.	Initial testing for electrospinning	78
6.4.	Electrospinning trial	79
6.5.	Preliminary electrospinning trial of PVA and graphene.....	82
6.6.	Electrospinning of PVA	85
6.7.	Electrospinning trial of PVA and graphene	90
6.8.	Introduction of graphene to PVA for electrospinning.....	100
6.9.	Optimisation of the electrospinning of PVA and graphene	102
6.10.	Discussion of electrospinning experiments	106
6.11.	Summary	108
Chapter 7	Results and discussion.....	109
7.1.	Instrumentation	110
7.2.	Results of the synthesis of graphene and graphene oxide	111
7.2.1.	Graphene oxide results	111
7.2.2.	Reduction of graphene oxide to form graphene	119
7.2.3.	Discussion of methods.....	130
7.3.	Results of the electrospinning of graphene fibres	131
7.4.	Summary	135
Chapter 8	Conclusions.....	136
Chapter 9	Future work.....	138
References		139

i. List of figures

Figure 3-1 The crystalline structure of graphene (top), fullerenes (bottom left), carbon nanotubes (bottom middle) and graphite (bottom right) [10]. Graphene is a 2D crystalline material composed of a monolayer of carbon atoms and it is the basic structural element of carbon nanotubes, fullerenes and graphite.	7
Figure 3-2 Fermi surface of graphene represented by E as a function of the wave number in the x-direction, k_x , and the wave number in the y-direction, k_y . The Fermi energy of graphene is indicated by the black line [13].	9
Figure 3-3 Energy band structure of single-layer graphene. The inset is an enlarged image of the area around the K point [20].	9
Figure 3-4 Energy band structure of bi-layer graphene. The inset is an enlarged image of the area around the K point [20].	10
Figure 3-5 The quantum Hall effect observed in graphene [18]. The plot indicates σ_{xy} of single-layer graphene as a function of the number of charge carriers, n (depicted in red) and the longitudinal resistivity, ρ_{xx} , of single-layer graphene as a function of n (depicted in green) in a uniform magnetic field at a temperature of 4 K. The inset depicts σ_{xy} of bi-layer graphene as a function of n [18].	11
Figure 3-6 The electric field effect in few-layer graphene. (A) depicts the resistivity of few-layer graphene, ρ , as a function of gate voltage, V_g , (the colours indicate the temperature in Kelvin: green = 5 K, blue = 70 K, orange = 300 K). (B) depicts σ as a function of V_g ; this was obtained by inverting the blue plot in (A). (C) depicts the Hall resistivity, R_H , as a function of V_g at 5 K [1].	12
Figure 3-7 HRTEM image of single-layer graphene. The bright spots indicate carbon atoms whereas the darker spots indicate gaps in the lattice [88].	21
Figure 3-8 TEM images of single-layer graphene (a) and multi-layer graphene (b) [79].	21
Figure 3-9 TEM images of (a) GO and its selected area diffraction (SAD) pattern (insert), and (b) graphene produced via the reduction of GO [74].	22
Figure 3-10 SEM images of (A) an individual flake of graphene and (B) multiple graphene flakes [12].	22

Figure 3-11 SEM image of graphite [79].	22
Figure 3-12 Raman spectra of bulk graphite (bulk – green), 3-layer graphene (3LG – blue), bi-layer graphene (2LG – red) and single-layer graphene (1LG – black) measured with laser excitation of 633 nm (note that the spectra have been normalised to have the same G peak intensity) [4].	24
Figure 3-13 Raman spectrum of GO using 514 nm laser excitation. The D and G peaks are located at 1590 cm^{-1} and 1350 cm^{-1} , respectively [12].	25
Figure 3-14 Raman spectra showing the change in the G (a) and 2D (b) peaks as a function of the number of layers of graphene for 633 nm laser excitation [91].	25
Figure 3-15 Raman spectra for graphite (red) and single-layer graphene (blue) using a 532 nm laser excitation [96].	26
Figure 3-16 AFM image of graphene oxide [12].	27
Figure 3-17 AFM image of graphene. The various colours in the image represent: dark red-brown (bottom right area) – silicon dioxide surface, red (central area) – graphene of 0.8 nm height, yellow-brown (bottom left section) – graphene of 1.2 nm height, yellow-orange (top left) – graphene of 2.5 nm height [1].	27
Figure 3-18 XRD patterns for graphite and graphene oxide (GO) [111].	29
Figure 3-19 XRD pattern of chemically reduced graphene samples [107].	30
Figure 3-20 (a - i) XRD patterns for graphene where the numeric value indicates the number of layers, (k) the combined XRD plot for all the graphene samples [112].	30
Figure 4-1 Taylor cone formation at the end of the spinneret [170].	42
Figure 4-2 Diagram of the two basic configurations of the electrospinning apparatus, a) vertical and b) horizontal [169].	42
Figure 4-3 Typical SEM image of electrospun graphene/PVA composite fibres [193].	51
Figure 4-4 SEM image of electrospun PVA with visible beading present [192].	51
Figure 4-5 SEM image of electrospun PVA depicting a web-like deposit [192].	51
Figure 4-6 FEG-SEM image of electrospun polystyrene/THF fibres with visible pores present [225].	51
Figure 5-1 GO produced via the Hummers' method prior to washing.	61
Figure 5-2 Solid GO collected following the filtration of GO produced via the Hummers' method. The various different colours of the solids indicate the area of the solution from which they were filtered: lightest yellow-brown solid (a) - upper part; light green-brown solid (b) - upper middle part; dark yellow-brown solid (c) – lower middle part; and dark brown-black solid (d) – lower part.	62
Figure 5-3 GO produced via the modified Hummers' method with extended oxidation time prior to washing. Side view (a) and top view (b).	62

Figure 5-4 GO obtained from the modified Hummers' method with extended oxidation time (a) after water wash and (b) after second ethanol wash.....	63
Figure 5-5 GO produced via the modified Hummers' method with additional KMnO_4 prior to washing. Side view (a) and top view (b).	63
Figure 5-6 GO produced from the modified Hummers' method as it appeared after the HCl wash (a) and after the final wash (b).	64
Figure 5-7 GO produced via the Tour method prior to washing, while stirring.	64
Figure 5-8 Yellow-brown solid obtained immediately after filtering.	65
Figure 5-9 GO obtained via the Tour method after the final ethanol wash.	66
Figure 5-10 GO solution upon the addition of 3.0 ml of H_2O_2 (a) and 6.0 ml (in total) of H_2O_2 (b).	66
Figure 5-11 Yellow-brown appearance of GO solution.	67
Figure 5-12 GO obtained via the Huang method after the last ethanol wash.	67
Figure 5-13 Colour change from the yellow-brown-colour of the GO solution (a) to the black colour following the reduction reaction via NaBH_4 (b) and the resulting filtered graphene (c).	69
Figure 5-14 GO solution from the Tour method (a); GO solution after addition of ascorbic acid (b); solution after 30 minutes ultrasonication (c); and solution after 90 minutes ultrasonication (d).	70
Figure 5-15 Molybdenum box to house the GO samples in the furnace.	71
Figure 5-16 GO films before (a) and after (b) thermal treatment.	71
Figure 5-17 GO solutions prepared using the GO from: (a) the Hummer's method, (b) the modified Hummers' method with extended oxidation time, (c) the modified Hummers' method with additional KMnO_4 , (d) the Tour method and (e) the Huang method.	73
Figure 6-1 Circuit diagram of the designed DC high voltage power supply.	76
Figure 6-2 The NE-1000 syringe pump used for electrospinning.....	76
Figure 6-3 Designed Perspex housing (a) and movable stage (b).	77
Figure 6-4 Assembled apparatus for electrospinning.....	77
Figure 6-5 SEM images of electrospun fibres produced from the 2 % (wt. /vol.) PVA solution at low magnification (a) and high magnification (b).	81
Figure 6-6 SEM image of large deposits produced from the electrospinning of PVA (2 %): GO (2:1).	81
Figure 6-7 SEM images of deposit of electrospun PVA [2%]: graphene (1:1) at low magnification (a) and high magnification (b).	82
Figure 6-8 SEM images of fibres produced from the electrospinning of PVA [10 %]: G (1:1) at low magnification (a) and higher magnification of the same area (b).	84

Figure 6-9 SEM images of fibres produced from the electrospinning of 4 % (wt. /vol.) PVA at 20 kV and 8 cm at low magnification (a) and high magnification of the same area (b).	86
Figure 6-10 SEM images of fibres produced from the electrospinning of 4 % (wt. /vol.) PVA at 22 kV and 10 cm at low magnification (a) and high magnification of the same area (b).	87
Figure 6-11 SEM images of fibres produced from the electrospinning of 6 % (wt. /vol.) PVA at 180 μ l/min and 3 cm at low magnification (a) and high magnification of the same area (b).	88
Figure 6-12 SEM images of fibres produced from the electrospinning of 6 % (wt. /vol.) PVA at 180 μ l/min and 15 cm at low magnification (a) and high magnification of the same area (b).	88
Figure 6-13 SEM images of fibres produced from the electrospinning of 10 % (wt. /vol.) PVA at 90 μ l/min and 15 cm at low magnification (a) and high magnification of the same area (b).	89
Figure 6-14 SEM images of fibres produced from the electrospinning of 12 % (wt. /vol.) PVA at 90 μ l/min and 15 cm at low magnification (a) and high magnification of the same area (b).	89
Figure 6-15 SEM image of the gold coated deposit produced from the electrospinning of 8 % (wt. /wt.) polystyrene/amy l acetate and graphene.	97
Figure 6-16 SEM image of the fibres produced via the electrospinning of 8 % (wt. /vol) PVA solution with graphene.	97
Figure 6-17 SEM image of the deposits produced via the electrospinning of 8 % (wt. /vol) PVA solution with graphene at a tip-to-collector distance of 5 cm.	98
Figure 6-18 SEM images of the fibres produced via the electrospinning of 10 % (wt. /vol) PVA solution with graphene at low magnification (a) and high magnification of the same area (b).	98
Figure 6-19 SEM images of the fibres produced via the electrospinning of 12 % (wt. /vol) PVA solution with graphene at low magnification (a) and high magnification of the same area (b).	99
Figure 6-20 SEM images of the fibres produced from Experiment I at low magnification (a) and higher magnification of the same area (b).	104
Figure 6-21 SEM images of the fibres produced from Experiment II at low magnification (a) and higher magnification of the same area (b).	104
Figure 6-22 SEM images of the fibres produced from Experiment III at low magnification (a) and higher magnification of the same area (b).	105
Figure 6-23 Uniform mixture of graphene suspended in a solution of PVA.	106
Figure 7-1 SEM images of graphite at low magnification (a) and higher magnification (b). ...	111
Figure 7-2 SEM images of the GO flakes produced from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO ₄ , the Tour method, and the Huang method, respectively.	113

Figure 7-3 TEM images of the GO flakes produced from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively.	115
Figure 7-4 XRD pattern for graphite.....	117
Figure 7-5 XRD patterns of the GO produced from each of the five experimental methods....	117
Figure 7-6 EDX spectrum from SEM for GO from Experiment 3.	118
Figure 7-7 EDX spectrum from SEM for GO from Experiment 4.	119
Figure 7-8 SEM images of GO reduced via NaBH_4 . Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively. ..	120
Figure 7-9 TEM images of the graphene produced using the NaBH_4 method from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively.	121
Figure 7-10 TEM image of graphene from Experiment 3 produced using the NaBH_4 method.	122
Figure 7-11 XRD patterns of graphene produced from Experiments 3 and 4 via the NaBH_4 reduction method. G3 indicates the XRD pattern of graphene from Experiment 3, and G4 indicates the XRD pattern of graphene from Experiment 4.	123
Figure 7-12 EDX spectrum from SEM of graphene produced from Experiment 3 via the NaBH_4 reduction method.	124
Figure 7-13 EDX spectrum from of graphene produced from Experiment 4 via the NaBH_4 reduction method.	124
Figure 7-14 TEM images of the graphene synthesised from GO via the ascorbic acid method at low magnification (a) and high magnification (b).	125
Figure 7-15 XRD pattern of graphene produced from Experiment 4 via the ascorbic acid reduction method.....	126
Figure 7-16 Multi-peak fitted XRD patterns for the graphene resulting from the chemical reduction of GO. G3 NaBH_4 and G4 NaBH_4 indicates the XRD pattern of the graphene produced from the GO from Experiment 3 and 4 respectively through the use of NaBH_4 . G AA indicates the XRD pattern of the graphene produced from the GO from Experiment 4 which was reduced via ascorbic acid.....	127
Figure 7-17 TEM images of the graphene synthesised from GO via the thermal treatment reduction method at low magnification (a) and high magnification (b).....	128
Figure 7-18 XRD pattern of graphene produced from Experiment 3 via the thermal treatment reduction method.	129

Figure 7-19 EDX spectrum from SEM of the graphene synthesised via the reduction of the GO from Experiment 3 using the thermal treatment reduction method with an exposure time of 1 hour.	130
Figure 7-20 EDX spectrum from SEM of the graphene synthesised via the reduction of the GO from Experiment 3 using the thermal treatment reduction method with an exposure time of 3 hours.....	130
Figure 7-21 SEM images of PVA fibres produced from the electrospinning of 6 % (wt. /vol.) PVA solution at 3 cm (a) and 15 cm (b).	132
Figure 7-22 SEM images of PVA/graphene fibres produced from the electrospinning of 12 % (wt. /vol.) PVA solution with graphene at 5 cm (a) and 15 cm (b).	132
Figure 7-23 SEM images of PVA fibres produced from the electrospinning of 6 % (wt. /vol.) PVA solution at 180 μ l/min (a) and 90 μ l/min (b).	133
Figure 7-24 SEM images of PVA fibres produced from the electrospinning of 4 % (wt. /vol.) PVA solution at 20 kV (a) and 22 kV (b).	133
Figure 7-25 SEM images of PVA fibres produced from the electrospinning of 4 % (wt. /vol.) (a), 10 % (wt. /vol.) (b) and 12 % (wt. /vol.) (c) PVA solutions.....	134
Figure 7-26 SEM images of PVA/graphene fibres produced via the electrospinning of 12 % (wt. /vol) PVA solution with graphene using the determined optimal parameters observed at low magnification (a) and high magnification of the same area (b).	135

ii. List of tables

Table 3-1 Typical Raman peak positions for graphite, GO and graphene using 514 nm laser excitation	23
Table 5-1 Reagents used in the Hummers' method experiment.	55
Table 5-2 Reagents used in the Modified Hummers' method with extended oxidation time.	57
Table 5-3 Reagents used in the Modified Hummers' method with additional potassium permanganate.....	57
Table 5-4 Reagents used in the Tour method experiment.	58
Table 5-5 Reagents used in the Huang method experiment.	59
Table 6-1 Parameters used for initial testing of electrospinning apparatus.....	78
Table 6-2 Parameters used for the electrospinning trial experiment.	80
Table 6-3 Materials used for the preparation of 4, 6 and 10 % (wt. /vol.) PVA solutions.	82
Table 6-4 Parameters used for the preliminary electrospinning trial of PVA and graphene.	83
Table 6-5 Materials used for the preparation of 12 and 20 % (wt. /vol.) PVA solutions.	85
Table 6-6 Parameters used for the electrospinning of PVA.	86
Table 6-7 Materials used for the preparation of 10 and 12 % (wt. /vol.) PVA solutions.	91
Table 6-8 Amount of graphene added to PVA solutions and resulting graphene concentration.	91
Table 6-9 Amount of graphene added to PVA solutions and resulting graphene concentration.	93
Table 6-10 Parameters used for the electrospinning of PVA and graphene solution.....	93
Table 6-11 Materials used for the preparation of the 8 % (wt. /vol.) PVA solution.	94
Table 6-12 Materials used for the preparation of 8 and 10 % (wt. /wt.) polystyrene/amyl acetate solutions.	95
Table 6-13 Amount of graphene added to polymer solutions and resulting graphene concentration.	95
Table 6-14 Parameters used for the electrospinning of polymer solutions and graphene.	96
Table 6-15 Parameters used for the electrospinning of 12 % (wt. /vol.) PVA solution and graphene.	103
Table 6-16 Summary of electrospinning experiments (green: successful attempts, dark green: best outcome and optimum parameters).....	107

Chapter 1 Introduction

Graphene is a single atomic layer of carbon atoms arranged in a benzene-ring structure and exhibits two-dimensional properties. This material was recently isolated and characterized by Andre K. Geim and Konstantin S. Novoselov in 2004 [1]. It is the basic structural element of other carbon-derived structures such as carbon nanotubes and fullerenes [1-3]. Graphene is a highly efficient conductor of both heat and electricity. The strength-to weight of this material is also exceptionally high. Graphene's high conductivity is directly attributed to its electronic structure and properties. These properties are influenced by the method of fabrication thereof. This leads to the key focus of this research: the production of graphene for use in several applications, which includes the fabrication of graphene fibres. The uses of graphene extend to a variety of industries, including the fields of life sciences; electronics; and chemistry.

The Materials Science Laboratory based at Electrical Engineering has recently produced graphene. Graphene is of interest due to its superior electronic, mechanical and optical properties which allow for its application in several fields which include energy-related applications [4], transistor technology [5], composite materials [6] and water purification [7]. The main interest of this graphene-related research is to leverage applications of graphene in electrical and electronic engineering. There have been an increasing number of studies centred on graphene in the past decade due to its exceptional properties in terms of electrical conductivity, optical transparency and mechanical strength. This is the first study of graphene to be conducted in Electronic Engineering within UKZN. The aim of which was to establish a reliable route through which to produce graphene so that this area of research could grow further from this starting, seed point.

The applications of graphene are to date in their early stages, however, extensive investigations are currently underway in order to bring these applications to fruition. In fact, the potential of graphene is so vast that the British government has funded a National Graphene Institute which was completed earlier last year (2015), and the European Union funded Graphene Flagship initiative was launched in 2013 whose primary objective is to develop graphene from a purely academic material into commercial technology within 10 years [8]. Extensive research has been conducted into graphene superconductors [4, 9] and the processing and properties of graphene transistors [10, 11], however the research surrounding graphene in the form of fibres is fairly sparse [5]. Hence, it was decided to attempt to fill this apparent gap in the graphene research.

This research aims to produce graphene composite fibre using a novel method, i.e. via electrospinning using a carrier polymer, in this case polyvinyl alcohol (PVA). The appeal of graphene/PVA composite fibre is that it potentially integrates the exceptional characteristics of graphene with that of conventional, polymer fibres to produce a material which exhibits a combination of these properties. The prospective applications of such fibre include conductive wire, photovoltaic cells, supercapacitors, and strengthening components [5].

There are a number of existing methods used to produce graphene, these include chemical vapour deposition [6] as well as mechanical [1] and chemical exfoliation [12]. The graphene produced for this research was synthesised using a chemical approach by first oxidising graphite ‘flakes’ to form graphene oxide and later reducing this to attain graphene via chemical as well as thermal reduction methods. The graphene oxide samples resulting from each of these methods were compared based on the degree of oxidation of each sample and the graphene produced was similarly analysed by comparing the degree of reduction (or deoxygenation) of the samples. The graphene fibres were produced using the electrospinning method of fabrication. The fibres fabricated using this technique were analysed through the use of microscopy techniques and the quality of the fibres were determined based on the morphology thereof.

An outline of the dissertation follows below:

Chapter 2 presents an overview of the discovery and history of graphene which is the material under investigation. This chapter highlights the various properties of graphene which have resulted in the extensive research surrounding this material. The methods used to synthesise and characterise graphene are also discussed, along with the plethora of applications of this material.

Chapter 3 discusses the process of electrospinning; this includes a detailed description of the process itself as well as the processing, solution and ambient parameters that each affect the eventual electrospun fibre morphology.

Chapter 4 details the first stage of the experimental work: the synthesis of graphene. Each of the methods used to synthesise graphene are detailed along with the various methods of reducing the graphene oxide that was produced. Observations that were made on the qualitative indications of the quality of the graphene oxide are also detailed in this chapter.

Chapter 5 details the second stage of the experimental work: the fabrication of graphene fibres. The graphene fibres were produced on a microscopic scale using electrospinning. The microscopic production of the graphene nanofibres involved the electrospinning of graphene together with a polymer material. The methodology is discussed and the conducted experiments are reported in detail.

Chapter 6 collates the results from Chapters 4 and 5 and presents these results together with an analysis and interpretation of the data that was collected from the experiments conducted over

the one-year research period. These results are in the form of transmission and scanning electron microscopy images, energy-dispersive X-ray spectra, as well as X-ray diffraction patterns.

Chapter 7 concludes this dissertation and presents the primary findings gleaned from this research. This chapter confirms the achievement of the objective of this research: a reliable method of producing graphene was established and graphene nanoscale fibres were successfully fabricated. This chapter also includes future work and recommendations that may be implemented.

Chapter 2 Aims and objectives

The key focus of this research was the production of graphene for use in several applications, which include the fabrication of graphene fibres. The research question for this work was, can a reliable graphene synthesis route be established in order to produce high quality graphene for various applications? High quality graphene here constitutes graphene with minimal topological defects and large surface area. As this is the first study of graphene to be conducted in Electronic Engineering within UKZN, the aim of this research was to establish a reliable route through which to produce graphene so that graphene-related research could thereafter grow and develop.

The secondary aim of this research was to produce graphene/PVA composite fibres through the electrospinning of graphene with a carrier polymer, which was PVA in this case. The potential applications of such composite fibre include conductive wire, photovoltaic cells, supercapacitors, and strengthening components [5].

In summary, the aims of this research were to synthesise graphene and graphene oxide, design and setup an electrospinning apparatus, and electrospin graphene fibres.

Chapter 3 Graphene and its applications

The question posed for this research is whether graphene can be fabricated into fibres for various applications; with the primary focus falling on the establishment of a reliable synthesis route through which to produce graphene. It is necessary to investigate the properties of graphene, hence a study of the various properties of graphene was conducted followed by an investigation of the methods of synthesising and characterizing this material; this review is presented in this chapter.

3.1. Discovery and brief history

Graphene has recently been isolated and characterized for the first time by Andre K. Geim and Konstantin S. Novoselov in 2004 [1]. The researchers were awarded the Nobel Prize in Physics in 2010. The full potential of this material is just beginning to be explored.

People have been unknowingly creating “pseudo” graphene each time they draw a pencil across a page. The ‘lead’ contained within a standard pencil actually consists of graphite, and graphite is essentially weakly bonded layers of graphene. Therefore when one draws a pencil across a page, thin layers of graphite are transferred to the surface of the paper - this is “pseudo” graphene or multi-layered graphene [13]. Prior to Geim and Novoselov’s pioneering work on graphene, Forbeaux and Oshima conducted experiments which resulted in the epitaxial production of graphene monolayers or films on various substrates [14, 15]; however it proved impractical to isolate the individual layers of the graphene itself, therefore it was difficult to characterize the material. Angular-resolved inverse photoemission spectroscopy was used to identify the multi-layer, crystalline graphitic material [14].

Prior to its discovery, it had been thought that a two-dimensional material consisting of merely a single atomic layer of carbon could not be stable at room temperature [16], yet Geim proved otherwise [1]. He was inspired by the work on carbon nanotubes at the time which prompted him to study “unfolded” carbon nanotubes [17]. This led him to produce graphene consisting of approximately 10 layers via the micromechanical exfoliation of graphite through the use of Scotch tape. This involved the iterative peeling off of the top layers of a thin sample of pyrolytic graphite until extremely thin films were left on the tape. The electronic properties of

these films were studied by Geim and his team which led to the eventual publication of the research paper entitled “Electric field effect in atomically thin carbon films” that earned him and Novoselov the Nobel Prize in Physics in 2010. In order to study the electronic properties of the graphene produced, the films were processed to make multi-terminal Hall bar devices which were placed onto an oxidized silicon substrate to which a gate voltage was applied [1]. Although these graphene films were only one atom thick, they remained stable at room temperature and displayed a very high mobility, μ , of its charge carriers [18]. The very first graphene sheets were later produced using improved approaches of Geim’s “Scotch tape” method. There are now several methods being used to produce graphene, including chemical vapour deposition, epitaxial growth and chemical oxidation of graphite to produce graphene oxide which is thereafter reduced to form graphene. These methods will be discussed in detail in Section 3.4.

3.2. Properties

3.2.1. Physical structure

Graphene was first isolated from a block of graphite via micromechanical exfoliation. Therefore, prior to discussing the physical structure of graphene, an understanding of its parent material, graphite, is required. Note that the synthesis of graphene itself will be further elaborated upon in Section 3.4. Graphite consists of a number of stacked single atomic carbon layers that are weakly coupled together, forming a 3D crystal lattice [14]. The sp^2 -hybridized carbon atoms of these 2D layers are arranged in hexagonal ring structures [19] - these single layers are what is known as graphene [10]. The crystalline structure of graphene is depicted in Figure 3-1. This shows that even though graphene comprises of merely single atomic layers, it displays long-range crystalline order [16]. The name “graphene” can also be applied to materials which contain up to 10 single atomic layers of carbon; however, the electronic state of graphene changes to become more similar to that of graphite as this 10-layer limit is approached [20].

Graphene is a 2D crystalline material as it is composed of a monolayer of carbon atoms, and it is the basic structural element of other carbon-derived structures such as carbon nanotubes as well as fullerenes [1-3]. Figure 3-1 illustrates this. Carbon nanotubes can in fact be thought of as graphene sheets which are rolled into 1D nanotubes and fullerenes as graphene sheets in a spherical structure [10]. Graphene may be considered “unzipped” carbon nanotubes since the walls of carbon nanotubes with diameters of ~ 1.2 nm are typically single atomic thick sheets of carbon [2]. Each of these carbon-based materials displays unique properties which make these individual structures (fullerenes, nanotubes, graphene and graphite) ideally suited for specific applications [10].

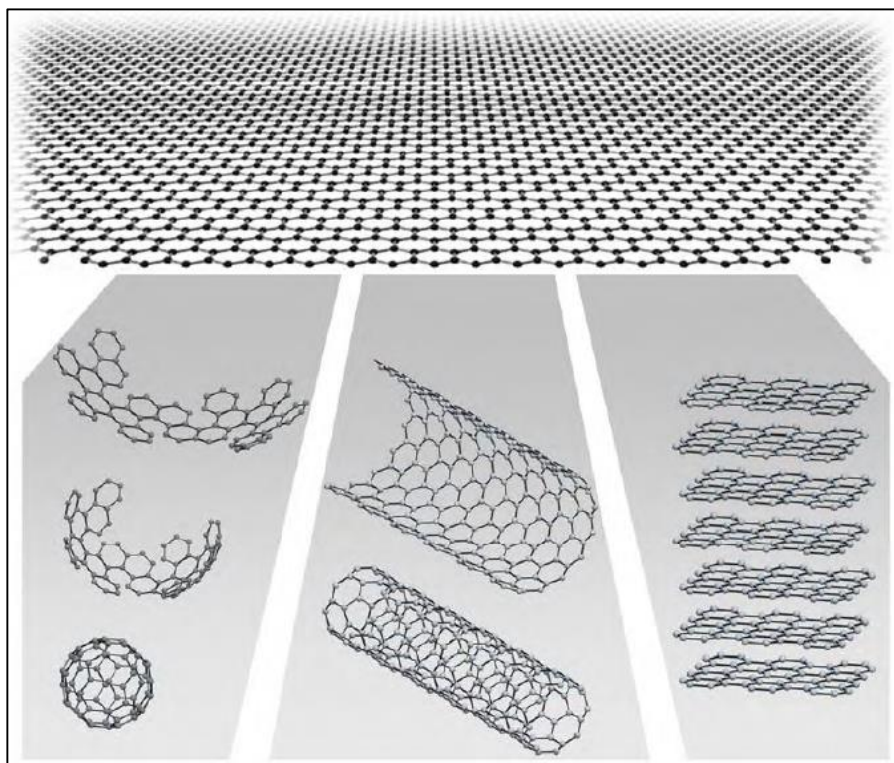


Figure 3-1 The crystalline structure of graphene (top), fullerenes (bottom left), carbon nanotubes (bottom middle) and graphite (bottom right) [10]. Graphene is a 2D crystalline material composed of a monolayer of carbon atoms and it is the basic structural element of carbon nanotubes, fullerenes and graphite.

3.2.2. Electronic structure and properties

Graphene has been described as both a 2D zero-overlap semimetal [1] as well as a zero-gap semiconductor [10]. The electronic properties of graphene were initially studied through the fabrication of Hall bar devices using graphene films to which a gate voltage was applied. This allowed the electronic properties of graphene to be characterised. The devices that were produced using thin, few-layer films of graphene displayed electronic properties typically associated with that of a 2D semimetal whereas the devices produced using thicker films of graphene displayed a combination of 2D and 3D electronic properties [1]. This is consistent with the observation that the electronic state of graphene changes to become more similar to that of graphite as the number of layers surpasses the 10-layer limit [20]. In fact, the electronic properties of single-, double- and few-layer graphene are distinctly different due to the presence of higher numbers of charge carriers in thicker layers of graphene [1, 21].

As mentioned, graphene is a zero-gap semiconductor, however this behaviour applies solely to single-layer graphene whereas graphene consisting of three or more layers displays distinct semi-metallic behaviour, akin to that of graphite [20]. Bi-layer graphene displays unique properties since it exhibits semimetal behaviour, however there is an overlap in its energy levels, although this overlap is extremely small [20].

The energy band diagram of single-layer graphene reveals that the conduction and valence bands intersect at the point where the energy, E , is zero i.e. $E = 0$. This is the location of the Fermi energy. Indicating that single-layer graphene is a zero-gap semiconductor [10]. The Fermi surface of graphene differs from that of 3D materials in that it consists of a system of six double cones [13]; shown in Figure 3-2. The Fermi level of intrinsic graphene is depicted by the circular black line in Figure 3-2. This level may be altered by doping the material through the application of an electric field [13]. The energy band diagram of single-layer graphene can be seen in Figure 3-3, which shows that the cosine-like energy bands of single-layer graphene intersect at the K point of the hexagonal Brillouin zone. The inset of Figure 3-3 indicates that the energy spectrum of single-layer graphene is linear around the Fermi level. The curvature of the conduction and valence bands is an indication of the effective mass, therefore linear behaviour suggests zero effective mass [13]. This phenomenon of zero effective mass is also echoed in Figure 3-2. The dispersion relation around the six double cones depicted in this figure is linear, thereby implying massless excitations [13]. In fact, the equation which is used to describe the energy of graphene is equivalent to that of the Dirac equation which is used for massless fermions travelling at a constant speed of 10^6 m/s [13]. It can be concluded that the charge carriers behave as massless Dirac fermions [18] and are described by the Dirac equation rather than Schrödinger's equation which is typically used to describe the electronic characteristics of most materials [22-25].

While these charge carriers abide by the laws of relativistic quantum physics, it is important to note that they are, however, not relativistic particles [17]. This phenomenon enables one to draw parallels between graphene and particle physics and thus enables these physical properties to be studied in greater detail through the study of graphene itself [13, 17]. Geim has in fact likened this massless behaviour of the conducting electrons in graphene to the Large Hadron Collider but on a far smaller scale. This enables these concepts in particle physics to be studied on a vastly smaller and cost-effective scale [26]. One such concept in particle physics includes Klein tunnelling, and graphene has allowed for the testing of this phenomenon [13, 25, 27]. The Klein paradox is defined as “the unimpeded penetration of relativistic particles through high and wide potential barriers” [25]. Much of this research falls beyond the scope of this dissertation, however it is interesting to note that graphene enables the Klein paradox to be tested. While direct testing of this theory through the use of elementary particles proved impossible [25].

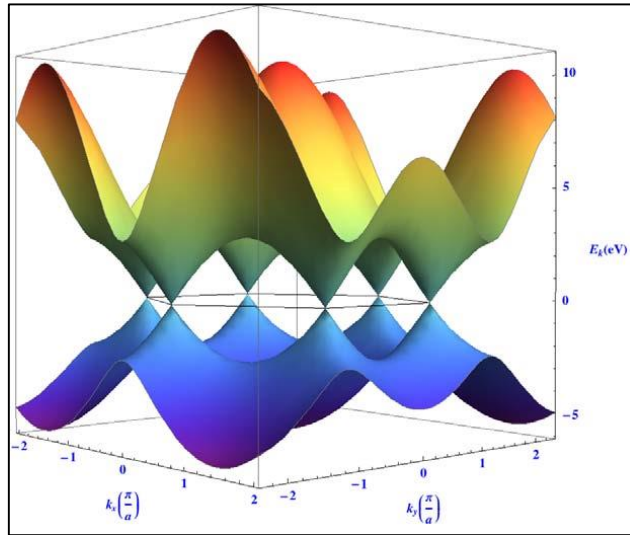


Figure 3-2 Fermi surface of graphene represented by E as a function of the wave number in the x-direction, k_x , and the wave number in the y-direction, k_y . The Fermi energy of graphene is indicated by the black line [13].

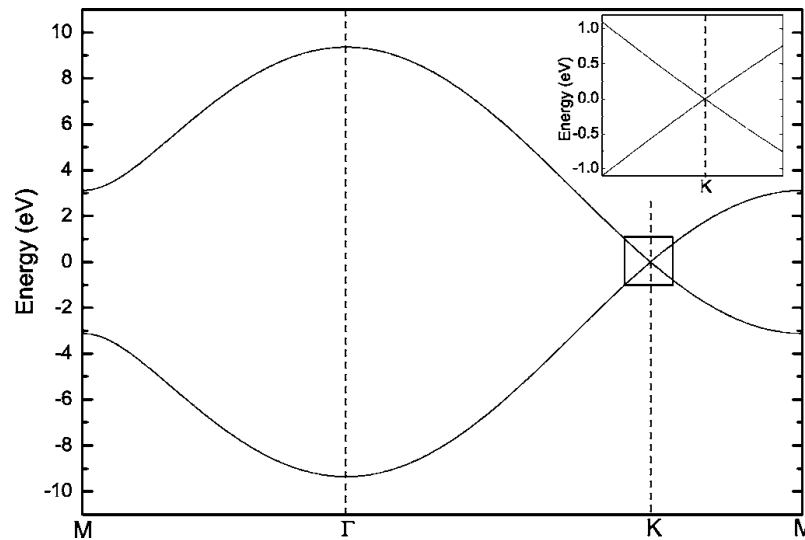


Figure 3-3 Energy band structure of single-layer graphene. The inset is an enlarged image of the area around the K point [20].

The energy band diagram of bi-layer graphene can be seen in Figure 3-4. There are a number of noticeable differences between this energy band diagram and the diagram depicted in Figure 3-3. In Figure 3-4, two levels are present rather than one, and the conduction and valence bands of these levels do not just intersect at the K point but rather overlap [20]. Also, the inset clearly shows that the spectrum is non-linear around this point but rather appears parabolic in nature. This overlap, although relatively small, in the conduction and valence bands which is apparent in bi-layer graphene is also a characteristic of bulk graphite [20]. This indicates that bi-layer graphene is considered a semimetal, similarly to graphite. With increasing number of layers in graphene, the band structure evolves to more closely resemble that of graphite. Once the number of layers exceeds 10, the band diagram of this material loosely termed “graphene” resembles that of graphite far more closely than that of single-layer graphene. Multi-layered

graphene exhibits a combination of 2D and 3D behaviour whereas bi-layer and few-layer graphene displays distinct 2D semimetal behaviour as seen in Figure 3-4 [1].

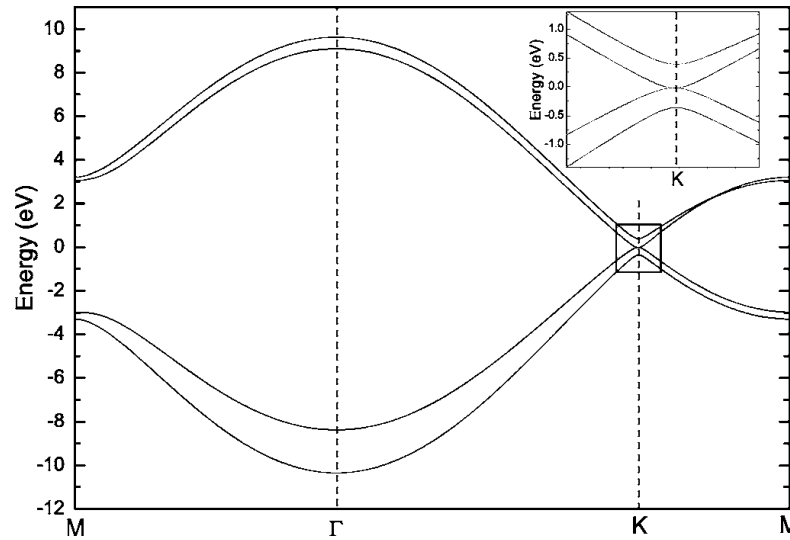


Figure 3-4 Energy band structure of bi-layer graphene. The inset is an enlarged image of the area around the K point [20].

Single-layer graphene also displays unique transport properties compared to those of bi- or few-layer graphene [20]. Due to the 2D nature of single-layer graphene, all the charge carriers are contained within this plane therefore the quantum Hall effect may be observed. Figure 3-5 depicts the Hall conductivity, σ_{xy} , of single-layer graphene as a function of the charge carrier concentration, n , in a constant magnetic field [18]. This figure indicates that the quantum Hall effect is inconsistent with that observed in conventional semiconductors since graphene displays a half-integer quantum Hall effect [18, 28]. The evidence of this is present in the period in which the quantum Hall effect plateaus occur. These plateaus are expected to occur at $\sigma_{xy} = \frac{4e^2}{h}N$, $N \in \mathbb{Z}$, however they occur instead at $\sigma_{xy} = \frac{2e^2}{h}(N + \frac{1}{2})$, $N \in \mathbb{Z}$ [18]. The presence of electron and hole Landau states at zero energy is the cause of this anomaly [29, 30]. Landau levels or states in quantum mechanics are the discrete, quantized energy levels that a charged particle may occupy in the presence of a uniform magnetic field [31]. It is important to note that this uncommon quantum Hall effect is not observed anymore as the number of layers increases from single-layer graphene to multi-layer [18]. Figure 3-5 also depicts this since the σ_{xy} of bi-layer graphene as a function of n in a constant magnetic field is plotted as well. Although in this case, the quantum Hall effect plateaus occur as expected at $\sigma_{xy} = \frac{4e^2}{h}N$, $N \in \mathbb{Z}$; this observed difference is due to the fermions in bi-layer graphene displaying non-zero mass at $n \approx 0$ and therefore do not behave as relativistic particles [18].

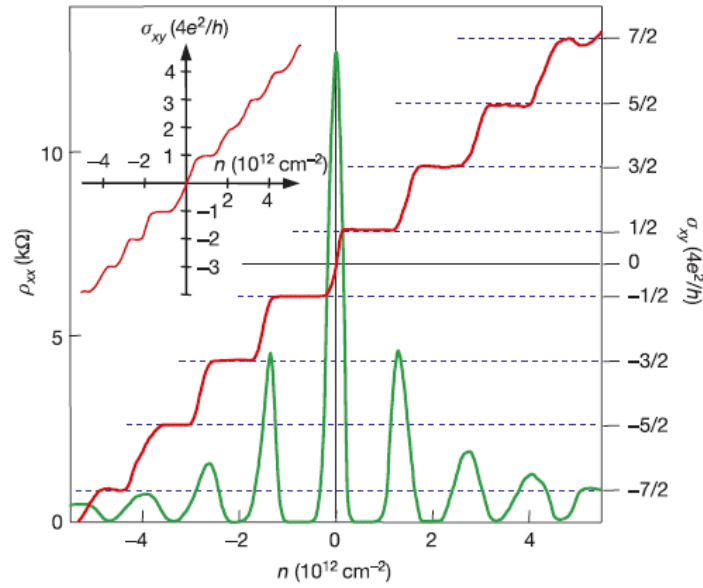


Figure 3-5 The quantum Hall effect observed in graphene [18]. The plot indicates σ_{xy} of single-layer graphene as a function of the number of charge carriers, n (depicted in red) and the longitudinal resistivity, ρ_{xx} , of single-layer graphene as a function of n (depicted in green) in a uniform magnetic field at a temperature of 4 K. The inset depicts σ_{xy} of bi-layer graphene as a function of n [18].

3.2.3. Conductivity

One of the primary factors as to why graphene has attracted significant recent attention over other 2D materials is its distinct ambipolar electric field effect [10]. This effect is especially notable in graphene since the charge carriers can be constantly tuned between electrons and holes in concentrations of $n \approx 10^{13} \text{ cm}^{-2}$ [10]. Under ambient conditions, the mobility, μ , of these charge carriers is in excess of $15\,000 \text{ cm}^2/\text{V}\cdot\text{s}$ [1, 18, 28, 32]. This is especially noteworthy since μ in graphene is exceptionally high for $n > 10^{12} \text{ cm}^{-2}$ in electrically- and chemically-doped devices [33]. This leads to the occurrence of ballistic transport in the range of micrometres at room temperature [21]. At length scales of the nano-range, electron transport becomes ballistic i.e. the length of the conductor becomes extremely small compared to the mean free path (the average distance that an electron travels prior to a collision with the lattice of the conductor) and the electrons travel without scattering [34]. Since the mean free path of electrons is relatively large, this implies reduced losses of energy.

In order to study graphene's electronic properties, Novoselov *et al.* processed few-layer graphene films into multi-terminal Hall bar devices that were placed on top of an oxidized silicon substrate to enable a gate voltage (V_g) to be applied [1]. Figure 3-6 (A) depicts the dependence of the sheet resistivity of the few-layer graphene (ρ) on the applied V_g . At the identical point of V_g where ρ displays its peak, Figure 3-6 (C) indicates that the Hall coefficient R_H displays a sharp reversal of its sign. This behaviour of graphene was very similar to the ambipolar field effect typical of semiconductors [1]. However, in graphene there is no zero-conductance area. The lack of a zero-conductance layer is caused by the pinning of the Fermi level inside the band gap, and

the electron transport is purely 2D. The primary findings of this paper can be seen in Figure 3-6. It shows that few-layer graphene may be modelled by a 2D metal with an extremely small overlap between its energy bands. This overlap decreases as the number of graphene layers is reduced [1].

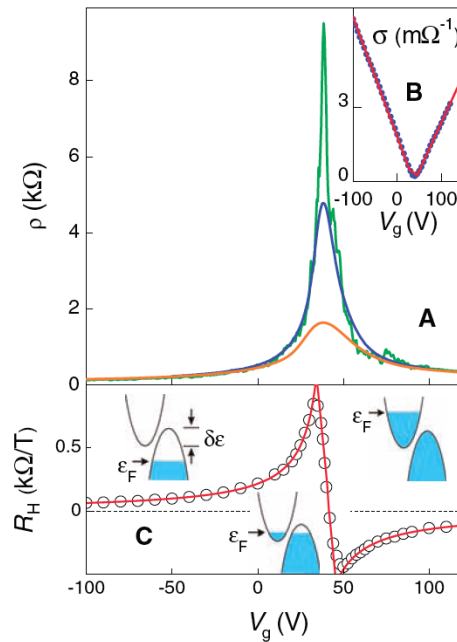


Figure 3-6 The electric field effect in few-layer graphene. (A) depicts the resistivity of few-layer graphene, ρ , as a function of gate voltage, V_g , (the colours indicate the temperature in Kelvin: green = 5 K, blue = 70 K, orange = 300 K). (B) depicts σ as a function of V_g ; this was obtained by inverting the blue plot in (A). (C) depicts the Hall resistivity, R_H , as a function of V_g at 5 K [1].

The electric field effect of a material allows its conductivity to be controlled, and this effect is the allure behind silicon since the field effect is pronounced in this material [35]. Due to the distinct ambipolar electric field effect, this then implies that graphene is a potential alternative or replacement for silicon transistors [11, 36]. This shall be elaborated upon in Section 3.6 on the applications of graphene. In addition, the electronic and conductive properties of graphene render it a possible candidate for applications in metallic transistors [1]. Graphene also offers several other desirable traits, such as ballistic transport [21], a linear current-voltage characteristic and sustainable currents greater than 10^8 A/cm² [1].

Now, considering that for any 2D material, its planar conductivity may be expressed as:

$$\sigma = en\mu \quad (3.1)$$

With μ being limited by acoustic phonons of $n = 10^{12}$ cm⁻² and therefore $\mu = 200\,000$ cm²/Vs, this leads to a 2D sheet resistivity of $31\,\Omega$ [13]. Converting this into the bulk conductivity for graphene results in $0.96 \times 10^6 \Omega^{-1} \text{cm}^{-1}$. This is higher than that of copper which is $0.60 \times 10^6 \Omega^{-1} \text{cm}^{-1}$ [13] which motivates this research to produce graphene for various applications. Although the conductivity of graphene may not be as high as that of superconductors, graphene provides the advantage of high conductivity at room temperatures. In addition, graphene is a superior thermal conductor as compared to copper since its thermal

conductivity was measured as $\approx 5\,000\text{ W/mK}$ whereas the thermal conductivity of copper is far lower at $\approx 401\text{ W/mK}$ [13]. Graphene is also capable of withstanding far higher current densities than copper [4] (10^8 A cm^{-2} vs 10^6 A cm^{-2} , respectively [4, 37]).

3.2.4. Mechanical properties

Graphene has been experimentally found to have an extremely high specific strength before breaking. This is a measure of strength (per unit area at failure) divided by density, before breaking. Graphene's specific strength is $48\,000\text{ kN m kg}^{-1}$ as compared to 154 kN m kg^{-1} for steel [4]. Strength tests were performed on single-layer, defect-free graphene to ascertain the intrinsic strength of the material. The intrinsic strength is defined as the maximum stress that can be supported by the material prior to failure in a pristine material without defects [38]. The intrinsic strength of graphene was determined using Atomic Force Microscopy deflection measurement techniques on suspended graphene sheets [39]. Single-layer graphene samples were tested. The samples were prepared from graphite crystals by mechanically depositing the graphite flakes over the substrate, single-layer graphene was selected using optical microscopy, and the thickness of the flakes was confirmed using Raman spectroscopy [38]. The samples were thereafter placed over open holes in a silicon substrate and clamped around the holes to stretch the films taught. Atomic force microscope nanoindentation was used to ascertain both the intrinsic strength and elasticity of the graphene films. The graphene single-layer samples were modelled as 2D membranes. The average value for the 2D Young's modulus, E_y , was determined as 342 N.m^{-1} with a standard deviation of 30 N.m^{-1} . This parameter can be expressed in 3D by dividing by the interlayer spacing of graphene's parent material graphite which is 0.335 nm [40] which yields $1.021 \times 10^9\text{ N.m}^{-2}$ [38]. The Young's modulus is a measure of a material's stiffness or elasticity and quantitatively provides an indication of the amount of strain that a material would experience for a given amount of stress in the elastic range. The value of E_y for the 2D material graphene is very high in comparison to that of other materials thereby indicating that this material is extremely stiff in nature, a hundred times more so than steel [13].

The study presented in [38] examined defect-free, single-layer graphene, however, graphene of this quality has currently only been produced in small quantities. Larger sheets of graphene are required for various applications, and these sheets are typically polycrystalline in nature. As a result, defects would be present in the form of grain boundaries and point defects. The study presented in [6] addressed this shortfall in the previous research in that the strength of large-area, polycrystalline graphene sheets synthesised via chemical vapour deposition (CVD) was investigated. Through the use of Transmission Electron Microscopy together with nanoindentation (using a similar method as that described above), it was concluded that the elastic stiffness of these graphene sheets produced via CVD was almost indistinguishable to that of defect-free graphene. There is only a slight reduction in strength due to the presence of grain

boundaries [6]. Although, extreme care has to be taken not to cause damage during post-processing of these sheets of graphene which would weaken it. This result is extremely significant since a large-area material such as graphene synthesised via CVD with an exceptionally high strength-to-weight ratio finds use in several applications including flexible conductors and strengthening of composite materials [6].

Carbon-derived fibres have been produced previously, however, graphene is superior to these carbon fibres as it has the ability to bend without causing damage to the fibre itself while carbon fibres are brittle in nature [41]. This is a highly attractive property in the context of this research since the objective is to produce graphene for the fabrication of graphene fibres. This property implies that graphene (or graphene fibres) may be used as flexible conductors in future applications. Carbon nanotubes have been processed to form high strength fibres with high electrical and thermal conductivities, however this is a costly and laborious process [5]. The production of graphene for the fabrication of graphene fibres offers a lower cost alternative and these graphene fibres may be used in several potential applications, such as in flexible supercapacitors and photovoltaic cells [5].

3.2.5. Other properties

Optical properties

Since a single sheet of graphene is only one atom thick it is an electron transparent material. It was found by Nair *et al.* [42], that graphene has an opacity of 2.3 ± 0.1 % thereby suggesting that the material is transparent. the opacity of the material increases proportionally to the number of layers, each layer adding 2.3 % to the opacity [42]. One would imagine that a material of minute thickness would absorb no incident white light, however, due to the electronic structure of graphene, some of this incident light is absorbed [42]. An average pane of ordinary glass transmits 80 – 90 % of incident light at best [43, 44] whereas graphene has been found to transmit 97 – 98 % of incident light [45]. The applications of such a material extends to solar panels, LCD screens as well as flexible touchscreens [19]. In fact, Samsung owns a number of patents relating to this area of graphene-based technology [4]. Much of the research on the optical characteristics falls outside the scope of this dissertation, therefore it shall not be expanded upon here.

Impermeability

Another property of interest of graphene-based material is its impermeability to all liquids, gases and vapours besides water [4, 46]. The tiny molecules of hydrogen and helium have been known to escape from almost any form of conventional vessel, however, graphene does not allow these molecules to pass through it [47]. The π -orbitals of the carbon atoms in graphene form an impenetrable, delocalized barrier [48] which essentially seals the spaces in its benzene-like rings thereby creating a repulsive field which prevents gas molecules from penetrating. This property

of graphene enables its application in gas separation and containment as well as in many other related applications.

The derivative of graphene, graphene oxide (GO) is very permeable to water [46]. Nair *et al.* speculated the following reasons behind this behaviour. The GO films contain 2D capillaries that contain a single layer of intercalating water under ambient conditions. Under low humidity conditions, the water between the layers evaporates and thus the interlayer spacing reduces proportionally. Therefore, this observed “capillary pressure” ensures that the surface of the GO film is constantly wet such that the permeability of the film is effectively determined by the surface evaporation [46]. Consequently, the membrane’s impermeability to other liquids and gases is attributed to the intercalating water molecules that prevent the permeation of other substances. Conversely, reduced GO is impermeable to water in addition to other liquids and gases since the interlayer spacing decreases significantly during the reduction process [46].

3.3. Synthesis of graphene

As previously mentioned, Geim and Novoselov are credited for first isolating and characterizing graphene. The method used to produce the graphene films is known as the “Scotch tape method” or more formally as micromechanical exfoliation of graphite. The mechanical exfoliation was performed by repeatedly peeling off thin layers of highly oriented pyrolytic graphite until films of few-layer graphene were attained on the tape [1]. The tape was then dissolved in a solution, leaving the graphene films behind. These films of only a few atomic layers of carbon were used to produce Hall bar devices which were placed onto an oxidized silicon substrate to which a gate voltage was applied [1]. This method demonstrated that single layers of graphene could be isolated and that graphene could be electrically characterized by studying these few-layer graphene samples.

Chemical Vapour Deposition (CVD) is another method through which graphene is synthesised. The process of CVD to produce graphene entails the growth of graphene films on a metal substrate such as copper or nickel in a high temperature furnace at temperatures of approximately 1000 °C [4, 10]. The carbon atoms provided by a hydrocarbon gas, such as methane, decompose from the carbon source and nucleate on the copper substrate. The nuclei then grow and develop into larger domains [4, 49, 50]. This method results in large-area polycrystalline graphene films. The copper substrate is preferential for growth of single-layer graphene while polycrystalline nickel is ideally suited for the growth of few-layer graphene. However, single- and bi-layer graphene can also be grown on nickel (111) substrates [51]. While the graphene grown via CVD contains grain boundaries, Lee *et al.* [6] showed that the strength of this material is comparable to that of pristine graphene. In order for the graphene films to be utilised in electronic devices, they must be processed by transferring them from the growth

substrate onto an insulating substrate such as silicon dioxide using a transfer polymer while the metallic substrate is etched away [52]. However, this process adversely affects the carrier mobility of the graphene produced, and the etched substrate cannot be reused. The method presented by Banszerus *et al.* [52] results in graphene grown on copper via CVD with minimal contamination during the transfer process thus improving the electronic properties of the CVD-graphene such that it is similar to that of exfoliated graphene. This method involved using a polymer stack prepared on a polydimethylsiloxane stamp which was covered with a flake of exfoliated hBN. The graphene on the copper substrate was picked up using this stamp due to the strong van der Waals interaction between the graphene and the hBN [52]. The graphene can then be transferred to another substrate.

Another, earlier method used to produce graphene is through epitaxial growth techniques. This method involves growing a single layer of graphene on a suitable single-crystal such as silicon carbide wafers through graphitization under high temperature (1440 °C) and vacuum conditions [14, 53, 54]. The silicon undergoes sublimation while the carbon undergoes graphitization under the high temperature treatment [14]. Alternative crystals upon which single layers of graphene may be epitaxially grown are iridium and nickel [15, 17]. The graphene produced via epitaxial growth exhibits properties which make it ideally suited for applications in electronics [54]. However, the combination of high cost and small wafer size might limit the widespread application of this approach [53].

While CVD and epitaxial growth techniques to synthesise graphene have resulted in large-area single-layer graphene films, the carrier mobility of the graphene produced via these methods remains lower than that of exfoliated graphene [52]. In addition, the graphene grown via CVD displays wrinkling due to a thermal mismatch between the copper substrate and the graphene itself. These wrinkles introduce further defects in the material thereby degrading its electronic properties [4]. Furthermore, the disadvantages of epitaxial growth techniques are the inherently high cost involved and the small size of the wafer substrates due to the single-crystal growth techniques [53]. While the graphene produced via this method may be ideally suited for electronic applications, it may not be suitable for larger-scale production of graphene for applications in other industries. The latter two methods discussed, CVD and epitaxial growth techniques, also require specialized equipment and toxic gaseous by-products are evolved during the CVD process [4].

The three methods discussed above are ideally suited for precise device assembly, such as for the production of electronic devices. However these approaches are not necessarily suitable for larger-scale manufacture of graphene [12]. Attaining graphene through chemically modified forms of graphite, such as graphene oxide (GO), provides a potentially cost-effective and large-scale method [53] through which to produce larger quantities of graphene [4].

3.3.1. Synthesis of graphene via chemical exfoliation

The most common approach towards attaining graphene from graphite is through graphite exfoliation. This can be achieved using mechanical means, as mentioned previously, or via chemical means. Chemical exfoliation involves the production of GO using strong oxidising agents. This method of synthesising graphene is investigated in detail in this dissertation as a means to produce large quantities of graphene.

The earliest approach to synthesize GO was developed by Brodie in 1859. This method involved the oxidation of graphite by potassium chlorate in fuming nitric acid [55]. Brodie's method was later improved upon by Staudenmaier in 1898 by using concentrated sulphuric acid (H_2SO_4) in addition to the reagents used by Brodie. Potassium chlorate was added in small amounts in multiple stages during the reaction [4]. This made the process simpler as well as less time consuming as it could then be performed in a single vessel [12]. The danger of both these methods was that hazardous gases, such as the explosive chlorine dioxide, were evolved during the oxidation reaction [56, 57]. Therefore these methods were further improved by Hummers and Offeman in 1958 where the reagents used were sulphuric acid (H_2SO_4), sodium nitrate (NaNO_3) and potassium permanganate (KMnO_4) instead [57]. By eliminating the use of potassium chlorate in the preparation of GO, the resulting experimental procedure could be executed quicker and with fewer hazardous byproducts [57]. However, the Hummers' method also involves the production of toxic gases, such as dinitrogen tetraoxide and nitrogen dioxide, and the yield of GO resulting from this method is low in comparison to alternative methods such as the Tour method [12]. Therefore, different experimental methods were investigated in order to produce larger amounts of highly oxidized GO by safer means. These methods make use of many of the Hummers' reagents with a few exceptions. These experimental methods will be expanded upon in Chapter 5 of this dissertation.

The chemical reactions which take place during the oxidation process introduce various functional groups to the sp^2 -bonded network of the graphite, namely hydroxyl or epoxide groups [58, 59] while carbonyl and carboxylic groups become attached to the edges [59, 60]. Pristine single-layer graphene flakes are ~ 0.34 nm thick while the thickness of a GO sheet is typically ~ 1 nm. The difference is due to the presence of the aforementioned functional groups as well as structural defects [45, 61]. Due to the presence of these functional groups GO is hydrophilic in nature and can be easily dispersed in water [62, 63] as well as in organic solvents [64, 65]. Due to the interruption in the π structure of the graphite by the addition of the functional groups resulting from the oxidation reaction, the strength of the van der Waals forces which hold the individual graphene layers together is reduced thereby allowing these layers to be separated under sonication in a solvent such as water [36]. The advantage of this property of GO is that it may be easily deposited onto suitable substrates to produce uniform, thin films and these films may be

used in electronic applications [66] following chemical reduction of the GO [45, 66-68]. However, GO is considered defective due to these functional groups which make it a nonconductive carbon material [57, 69, 70]. The electronic properties may be restored by reduction to produce graphene [60].

GO which has been prepared using the chemical exfoliation of graphite has many uses which include: the precursor in the preparation of graphitic films, a binding agent in the production of carbon products, as a constituent in lithium-ion batteries [71, 72] and for the production of various composites [73].

Reduction of graphene oxide

Following the chemical exfoliation of graphite to produce GO, graphene may be attained by reducing GO. The reducing agent serves to deoxygenate the GO and to reform the carbon-carbon double bonds [36]. There are numerous effective reducing agents which have been successfully employed to reduce GO, including hydrazine hydrate [63, 64] as well as anhydrous hydrazine [36] and sodium borohydride (NaBH_4) [74].

Gilje *et al.* [36] demonstrated that reduced GO (considered graphene) exhibits p-type semiconducting behaviour since the temperature versus resistance of the produced films revealed an inverse relationship. Also, the conductivity of the material increased when a decreasing voltage was applied to the fabricated FET devices. This is consistent with the expected electronic behaviour of single- and few-layer graphene as described in Section 3.2.2.

While the conductivity of GO is significantly increased following chemical reduction of GO to form graphene [36, 75, 76], the conductivity of the graphene produced has been shown to fall behind that of pristine graphene by a factor ranging from 10 to 10^2 [11, 77]. This apparent difference in conductivity is due to vacancies and residual functional groups, introduced during the oxidation process which are not entirely removed during chemical reduction [78]. These defects degrade the electronic properties of the graphene when compared to mechanically exfoliated graphene [79], therefore an alternative method was developed which preserved these desirable properties. This method is detailed in the following section. However, Gómez-Navarro *et al.* [78] showed that the largest area (~60 % constituting 3 – 6 nm) of the graphene synthesised via the reduction of GO consists of defect-free single-layer graphene similar to that produced via mechanical exfoliation methods, and that the defects present do not adversely affect the long-range orientational order. Although, these regions of defect-free graphene are bonded with defective clusters which result in numerous topological defects following the chemical reduction process [78]. However the effect of the inclusion of these defective clusters is not detrimental to the desired conductive properties of the graphene [63].

The reduction of GO through the use of various reducing agents which were employed during this research will be expanded upon in Chapter 5.

3.3.2. Synthesis of graphene via ultrasonic exfoliation

Graphene can also be obtained through the ultrasound assisted exfoliation of graphite in a suitable organic liquid such as N-methyl-pyrrolidone [79], dimethylformamide [79], and glycerol [80]. This liquid phase exfoliation of graphite produces graphene which is defect-free and as such maintains its electronic properties [79]. The liquids that are most suitable for the liquid phase exfoliation of graphite are those having a surface tension of 40 mN/m since these liquids allow the graphite flakes to be easily dispersed throughout the solvent rather than adhering to adjacent flakes [60, 79]. The liquid phase exfoliation method consists of three stages: the dispersion of the graphite in an organic solvent, the ultrasonic assisted exfoliation stage, and the decontamination stage [4]. The last stage involves the removal of the exfoliated graphite from the solvent as well as the separation of the exfoliated graphite flakes from the un-exfoliated flakes, which can be achieved through multiple washes with the aid of a centrifuge [4]. Raman spectroscopy of graphene produced using this method reveals that the graphene produced has very few defects and is therefore of a high quality [79].

Solvents such as N-methyl-pyrrolidone and dimethylformamide can be toxic if handled incorrectly [81, 82], and, furthermore, these solvents have high boiling points therefore it is not prudent to remove them via evaporation [4]. Alternatives with lower boiling points such as acetone, chloroform and isopropanol [4, 83] may be used to simplify the purification stage.

3.4. Methods of characterising graphene

Graphene may be characterized using several methods which include Scanning and Transmission Electron Microscopy (SEM and TEM, respectively), Raman Spectroscopy, Atomic Force Microscopy (AFM), and X-Ray Diffraction (XRD). These methods will be briefly discussed in this section which includes the expected results for graphene, graphene oxide and graphite. Note that the graphene produced for the purposes of this research was synthesised primarily via the chemical exfoliation of graphite therefore focus will predominantly lie on presenting the methods of characterizing the products from this process (unless otherwise stated), i.e.: graphite, GO and chemically reduced GO which is referred to as graphene.

Scanning and Transmission Electron Microscopy (SEM and TEM)

SEM and TEM provide insight into the structural features and defects of graphene [4]. Novoselov *et al.* [1] found that graphene films of thicknesses less than ~ 1.5 nm were no longer visible using optical microscopy and, therefore, AFM and electron microscopy were required to examine these samples.

TEM imaging techniques involve the transmission of a beam of electrons from a heated tungsten filament through thin samples, generally in the order of nanometres. The formation of

the image results from the interaction of the transmitted electrons with the specimen under inspection [84]. This interaction may result in the uninhibited passage of the electrons through the sample, the scattering of the electrons without energy loss, or the inelastic scattering of the electrons [84]. The third interaction may result in the formation of secondary electrons. The contrast of the image is achieved by preventing these secondary electrons from contributing to the image [84]. The image can then be magnified and is focused onto a fluorescent screen, atop a photographic film or it is detected by a sensor. The operator of the TEM may control the diameter of the apertures through which the electrons pass. This controls the intensity and angle of convergence of the electron beam [84]. The TEM operator can also control the focus, magnification, brightness and contrast of the image [84].

Images produced using the SEM are formed in a different manner to those formed using the TEM. The SEM makes use of a much finer beam of electrons for imaging of specimens. The electrons are also emitted from a heated tungsten filament. The specimen is scanned by the beam in a series of lines and frames [85]. Similarly, the interaction of the scanning electrons with the samples results in the formation of an image [86]. The electrons may be elastically reflected, absorbed by the sample resulting in the formation of low-energy secondary electrons, or they may be absorbed by the sample and emit visible light [85]. The main interaction responsible for image formation is that involving the development of low-energy secondary electrons [85], also called backscattered electrons [86]. A specialized secondary detector is used to detect the secondary electrons and thereby produce a resulting image of the specimen surface [85]. This image is essentially a map of the intensities of the emitted electrons from the scanned specimen area. The SEM operator can control the operating voltage of the SEM, as well as the focus, magnification, brightness and contrast of the image [85]. Scanning electron microscopy gives an indication of the surface topography and composition of the sample.

TEM is typically used to obtain images of materials in the order of nanometres. Graphene consists of a mono-layer of carbon atoms, and TEM enables the atomic features of this material to be investigated [87]. Although, at low operating voltages of the electron beam, the resolution of the image is limited whereas at higher resolutions, the operating voltage required is similarly higher. This can result in damage to the sample under inspection [87]. However, Meyer *et al.* [88] were able to obtain High Resolution TEM (HRTEM) images of graphene membranes at 1 Å resolution through the use of aberration-correction (spherical aberration tuned to $C_s = -17 \mu\text{m}$) together with a monochromator at comparatively low operating voltages (80 kV). This enabled the crystalline lattice as well as the structural defects of the graphene to be observed [88] as seen in Figure 3-7 below. Imaging technology such as this is vitally important in graphene research since it enables topological defects to be identified prior to incorporation into electronic devices. As mentioned earlier in this chapter, these defects alter the electronic properties of graphene therefore they must be identified prior to device production.

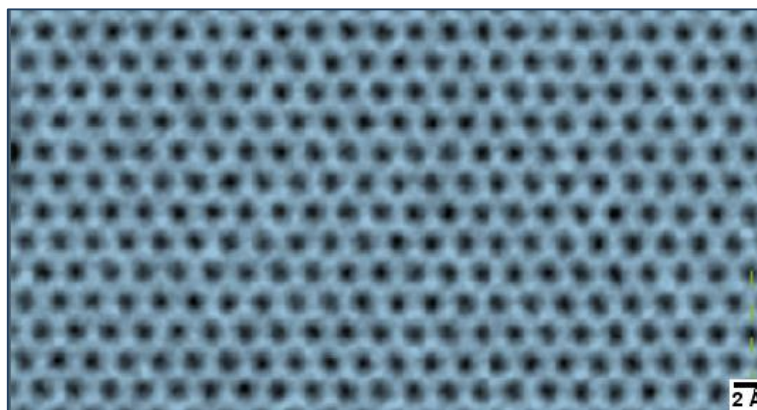


Figure 3-7 HRTEM image of single-layer graphene. The bright spots indicate carbon atoms whereas the darker spots indicate gaps in the lattice [88].

TEM and high resolution transmission electron microscopy (HRTEM) images of graphene typically reveal a flat, smooth surface and appear transparent. TEM images of pristine single- and multi-layer graphene can be seen in Figure 3-8.

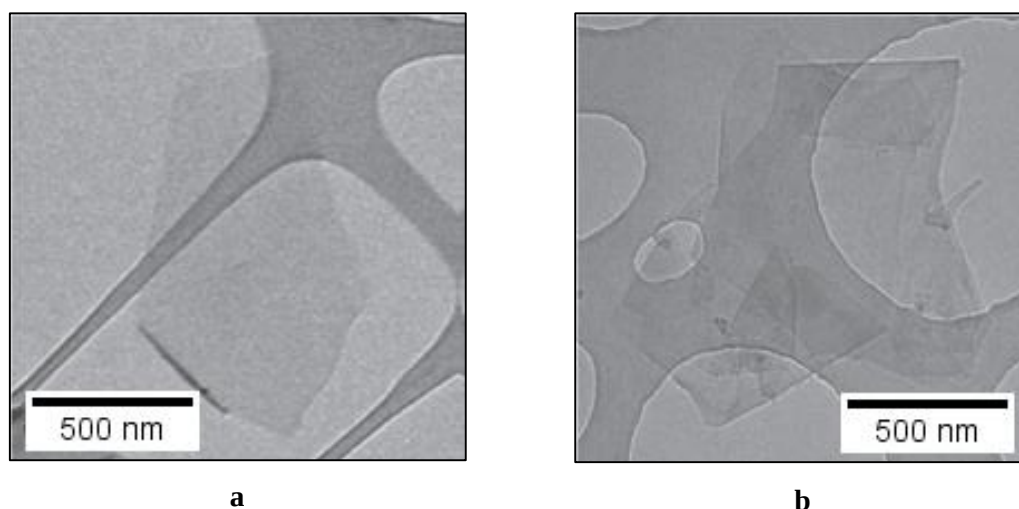


Figure 3-8 TEM images of single-layer graphene (a) and multi-layer graphene (b) [79].

TEM images of GO are similar to those of graphene. Figure 3-9 (a) below shows a typical image of a GO sheet supported on a lacey-carbon grid. The insert shows the selected area diffraction (SAD) pattern for GO. A TEM image of graphene produced via the reduction of GO can be seen in Figure 2-9 (b). The image reveals that the graphene produced following the chemical reduction of GO appears to be more rough and smaller in size than that of GO. This is caused by the atomic rearrangement as a consequence of the chemical reduction [74].

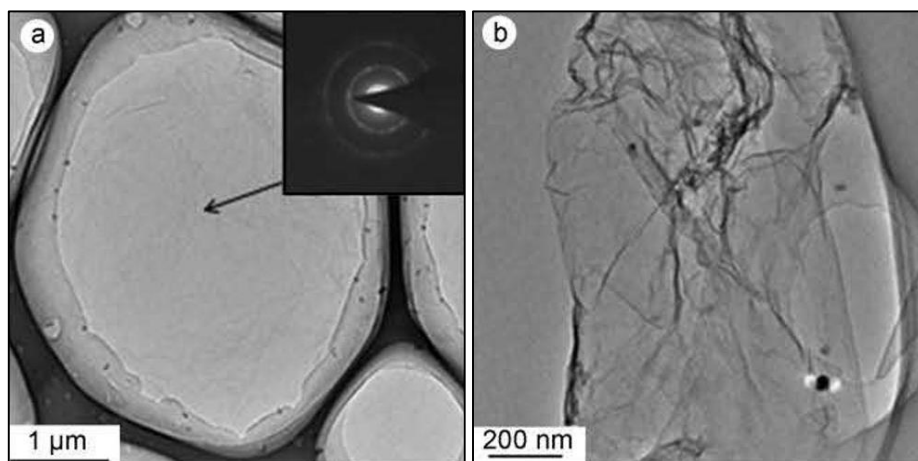


Figure 3-9 TEM images of (a) GO and its selected area diffraction (SAD) pattern (insert), and (b) graphene produced via the reduction of GO [74].

SEM enables the surface of the graphene flakes to be observed. One such image is depicted in Figure 3-10 (A). This graphene was synthesised via the Tour method. The surface of graphene appears smooth and uniform and the flake depicted below is approximately 60 μm in diameter. Figure 3-10 (B) shows multiple flakes of graphene which range in diameter from several micrometres up to 160 μm [12]. When compared to the SEM image of graphite, as presented in Figure 3-11, the graphene flakes appear markedly different. The graphene flakes appear far smoother and smaller in size than the graphite flakes.

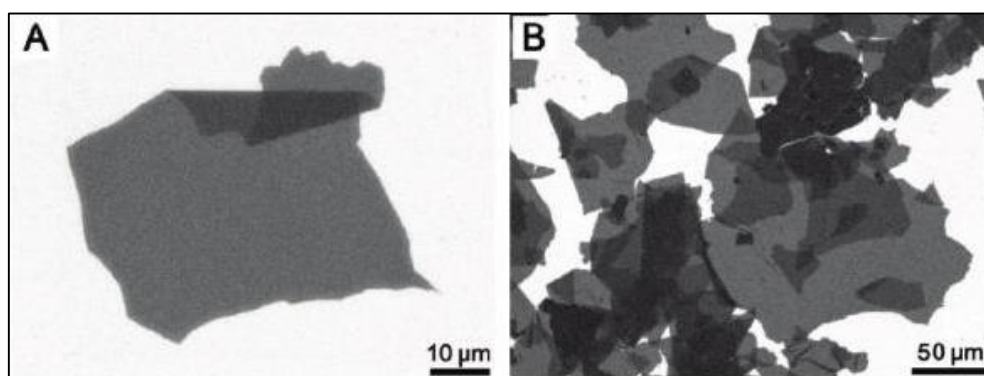


Figure 3-10 SEM images of (A) an individual flake of graphene and (B) multiple graphene flakes [12].

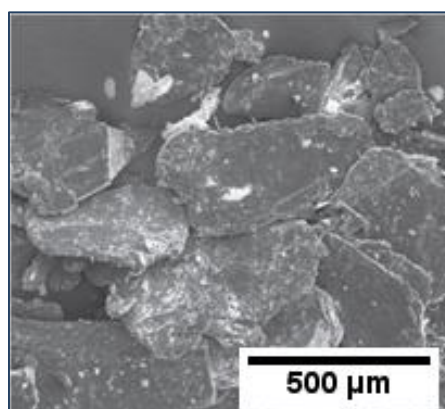


Figure 3-11 SEM image of graphite [79].

Raman Spectroscopy

Raman Spectroscopy offers a non-destructive, systematic approach to distinguish single-layer graphene from bi- and few-layer graphene [89-91]. This method of spectroscopy makes use of a monochromatic laser which is incident upon the sample under inspection. The molecules of the sample interact with this incident radiation thereby causing an upward or downward shift in the frequency of the radiation and this change in energy is identified by the detector [92]. Since graphite was first characterised using Raman spectroscopy, it has become the preferred method with which to analyse various carbon-based structures, including graphene, graphene oxide, carbon nanotubes and amorphous carbon [93]. The Raman spectrum of graphene provides insight into the electronic structure of graphene. This spectrum is distinctly different for increasing numbers of layers of graphene due to the change in the electron bands [90]. The characteristics of interest in the Raman spectra of graphene, GO and graphite are the G, D and 2D peaks. The G peak corresponds to the doubly degenerate phonon mode at the centre of the Brillouin zone [94]. The D peak is related to the disorder of the sample. It is caused by the breathing modes of the rings formed by the carbon atoms and is only present when there are defects within the sample [89, 90]. The 2D peak is the D peak overtone or second order [90, 91]. These peaks vary in form, position and intensity as the number of graphene layers change and this change is a reflection of the electronic band structure and electron-phonon interactions of the graphene sample under consideration [91]. The typical peak positions of the G, D and 2D peaks for graphite, GO and graphene using a laser excitation of 514 nm is shown in Table 3-1. Note that the D peak is absent in graphite and the 2D peak is absent in GO.

Table 3-1 Typical Raman peak positions for graphite, GO and graphene using 514 nm laser excitation

Peak	Peak position (cm ⁻¹)		
	Graphite	GO	Graphene
G	1580	1350	1580
D	-	1590	1350
2D	2700	-	2700

Figure 3-12 shows the Raman spectra for graphite as well as graphene consisting of various numbers of layers. It can be seen that the 2D peak in these spectra evolves with the number of layers of graphene. The 2D peak is an indication of the electronic band structure of the sample. In single-layer graphene, this manifests as a single peak whereas it distinctly changes as the number of layers increases [90]. Even bi-layer graphene is easily distinguishable from single-layer graphene as a shoulder is present in the 2D peak of the bi-layer Raman spectrum [95]. As the number of layers of graphene increases, the 2D peaks splits into a number of modes which overlap to form the peaks as seen in Figure 3-12 [96]. The G peak is also subject to a small shift as the number of layers increases [96], however, this shift is not nearly as noticeable as the shift

of the 2D peak. The D peak is not present in the Raman spectrum of graphene unless there are defects in the lattice structure [97]. Another defining characteristic which differentiates few-layer graphene from single-layer graphene is the C peak which is an indication of the interlayer coupling and probes the number of layers of graphene [4, 98, 99]. This peak is present in all the spectra depicted in Figure 3-12 with the exception of single-layer graphene. It appears at a shift of approximately 44 cm^{-1} in graphite and changes position slightly and decreases in intensity in few-layer graphene.

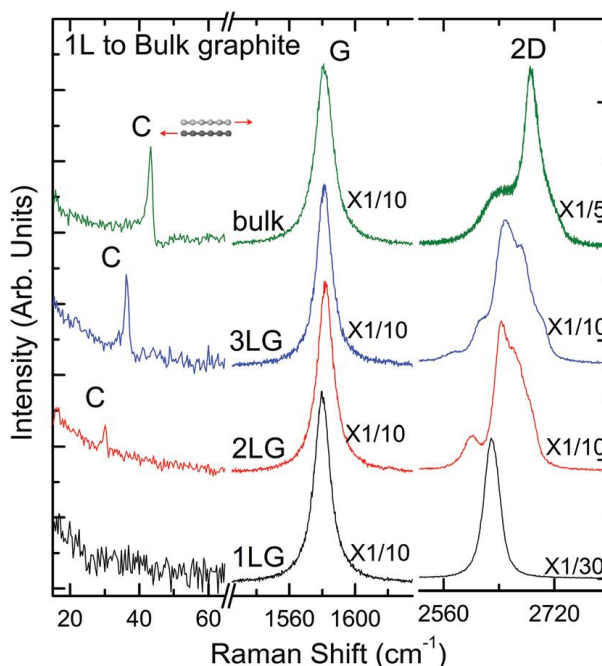


Figure 3-12 Raman spectra of bulk graphite (bulk – green), 3-layer graphene (3LG – blue), bi-layer graphene (2LG – red) and single-layer graphene (1LG – black) measured with laser excitation of 633 nm (note that the spectra have been normalised to have the same G peak intensity) [4].

The reduction of GO to produce reduced GO (here named graphene) can be confirmed using Raman Spectroscopy [36]. Stankovich *et al.* [63] observed a significant change of the spectrum of GO after being reduced via hydrazine. This confirmed that the GO was successfully deoxygenated and electrical conductivity room-temperature measurements confirmed that the electrical conductivity of the material was restored through the reduction process. If significant defects have been introduced during the oxidation and reduction processes, the Raman peaks will appear attenuated, indicating that the resulting product resembles amorphous carbon [100]. Marcano *et al.* [12] showed that for graphene synthesised via the Tour method, the D and G peaks were located at 1590 cm^{-1} and 1350 cm^{-1} respectively, for a laser with a wavelength of 514 nm. This suggests that lattice defects are present as expected [97]. The Raman spectrum for GO can be seen in Figure 3-13 below. The 2D peak of the Raman spectrum of graphene produced via the reduction of GO is also analysed to determine the number of layers in the sample [45]. The spectrum of this graphene differs from that of graphite and pristine graphene in that the D peak is

present – this indicates the presence of defects in the form of residual functional groups on the carbon lattice [45].

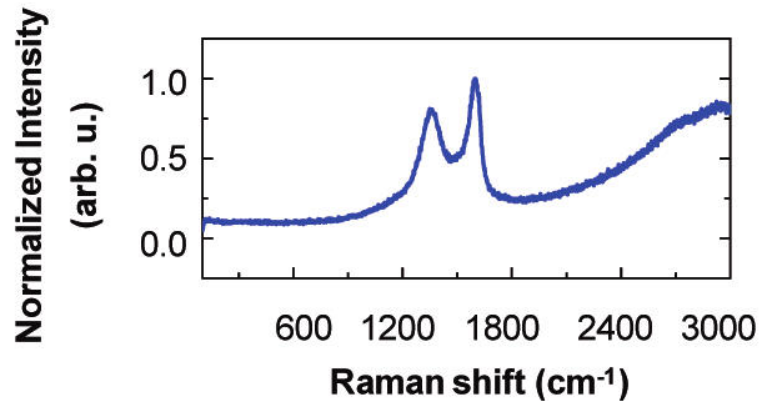


Figure 3-13 Raman spectrum of GO using 514 nm laser excitation. The D and G peaks are located at 1590 cm^{-1} and 1350 cm^{-1} , respectively [12].

As mentioned previously, the G and 2D peaks of the Raman spectra of graphene experience a change in position as the number of layers increases, this is highlighted in Figure 3-14. It can be seen clearly in Figure 3-14 (a) that the spectrum for 5-layer graphene is very similar to that of graphite and that the spectrum for 10-layer graphene is indistinguishable from that of graphite [91]; Figure 3-14 (b) also shows similar findings for the 2D peak. This is as expected since the electronic structure of $10 >$ layer graphene is more similar to that of graphite than to single-layer graphene [20].

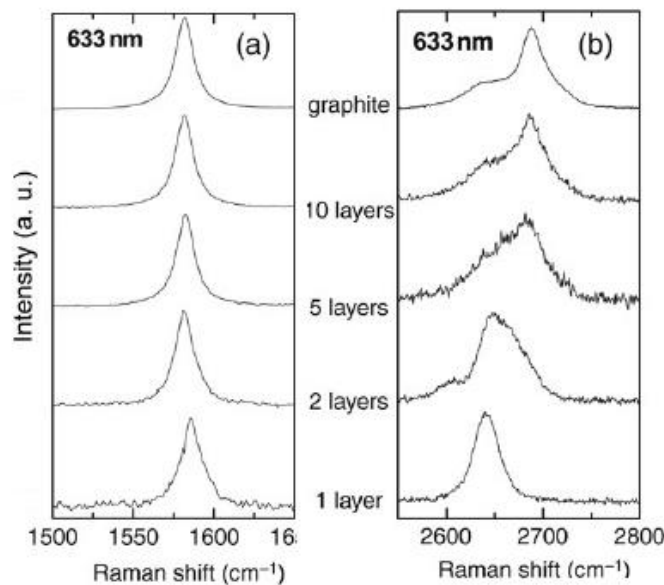


Figure 3-14 Raman spectra showing the change in the G (a) and 2D (b) peaks as a function of the number of layers of graphene for 633 nm laser excitation [91].

The Raman spectrometer which is available for use at the UKZN Westville Campus utilises a laser with a wavelength of 532 nm therefore, the following measurements have been included so as to provide the expected results when using this instrument. In the Raman spectrum of

graphene when using a 532 nm laser excitation, the G, 2D and D peaks occur at approximately 1580 cm^{-1} , 2690 cm^{-1} and 1350 cm^{-1} , respectively [95, 96, 101], as can be seen in Figure 3-15. The 2D and D peaks in particular are sensitive to variations in the excitation energy of the laser and are therefore located at slightly different locations when using lasers of different wavelengths [96]. The 2D peak of graphene is noticeably more intense than the G peak of its spectrum. This large difference in intensity of the two peaks is not present in the Raman spectrum of graphite [91].

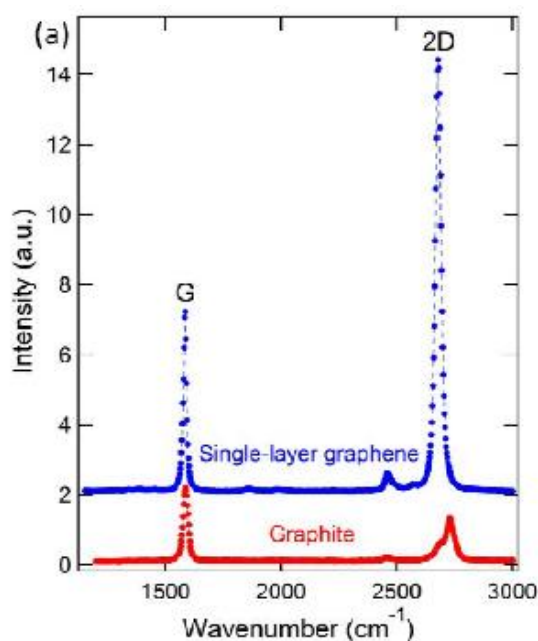


Figure 3-15 Raman spectra for graphite (red) and single-layer graphene (blue) using a 532 nm laser excitation [96].

Raman spectroscopy may be used to analyse the level of doping of a particular graphene sample [91] in addition to the previously mentioned uses. This lies outside the scope of this research, however may prove essential in further graphene-related research conducted in the Material Science Laboratory.

Atomic Force Microscopy (AFM)

Novoselov *et al.* [1] used optical microscopy to locate the regions of single- and few-layered graphene in their graphene samples. AFM was used to confirm the thickness of these regions [36]. AFM provides surface scanning of a sample in the nanometer range. Since graphene consists of merely a single layer of carbon atoms, this imaging technology, together with HRTEM, is ideal to analyse graphene samples [4].

In addition, tapping mode AFM allows the thickness of a particular sample to be measured [102]. AFM provides a height profile of the sample under inspection. An average thickness of the sample may be estimated from this data. In this way, AFM analysis enables the number of graphene layers in a particular sample to be estimated by dividing the average thickness of the sample by the interlayer spacing of graphite [60] which is $\sim 3.35\text{ \AA}$ [1]. The thickness of a typical

GO film is expected to be approximately 1 nm due to the presence of various functional groups [74], whereas the thickness of single-layer graphene is approximately 0.6 nm [87]. Therefore, pristine graphene may be differentiated from GO using AFM. Figure 3-16 and Figure 3-17 below depict AFM images of GO and graphene respectively. It is evident that the flakes of both materials appear to be smooth with irregular edges. The height of the GO depicted in Figure 3-16 was determined to be 1.1 nm [12] while the graphene depicted in Figure 3-17 consists of a few layers of graphene therefore the sample contained regions of varying heights (0.8 – 2.5 nm) [1]. As mentioned previously, the thickness of the GO flakes is greater than that of the graphene flakes due to the presence of functional groups. The discrepancies in the heights of the various regions in Figure 3-17 can be attributed to regions of single- and few-layer graphene.

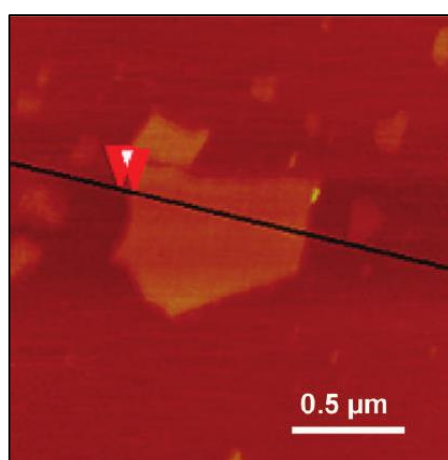


Figure 3-16 AFM image of graphene oxide [12].



Figure 3-17 AFM image of graphene. The various colours in the image represent: dark red-brown (bottom right area) – silicon dioxide surface, red (central area) – graphene of 0.8 nm height, yellow-brown (bottom left section) – graphene of 1.2 nm height, yellow-orange (top left) – graphene of 2.5 nm height [1].

X-Ray Diffraction (XRD)

XRD is a non-destructive process used to determine the crystalline structure of a material at the atomic level through the use of electromagnetic radiation [103]. This process entails an incident electromagnetic wave directed onto the sample under analysis. The detector of the diffractometer is rotated about the stage to capture the directions as well as intensities of the diffracted waves [104]. The sample under inspection is usually in powder form with average flake

size of $\sim 10 \mu\text{m}$ or smaller [105]. Due to the atomically periodic nature of most materials, this results in a distinct XRD pattern unique to each material [105]. XRD is a relatively simple approach used in the study of graphene to glean information on the interlayer spacing and thickness of graphene samples as well as an estimate of the number of layers in a particular sample [106]. Nazari *et al.* [107] showed that GO and graphene produced via different routes yield XRD patterns which vary slightly therefore the XRD patterns presented in this section are restricted to those which are relevant to this research.

The principle of XRD is based on the phenomenon of constructive interference that occurs when the incident X-rays encounter the crystalline sample. The X-rays are generated from a cathode ray tube source, such as a $\text{CuK}\alpha$ X-ray source, the X-rays are filtered by a monochromator, the monochromatic X-rays are then collimated to concentrate the rays, and the concentrated rays are directed towards to sample under inspection [108]. When the geometry of the X-ray incident on the sample satisfies Bragg's Law, this interaction results in constructive interference as well as a diffracted X-ray [109]. This law relates the spacing between planes in a particular crystal to the angle at which the X-rays are diffracted when they encounter the surface of the crystal [108]. The Bragg's Law equation is given by equation 3.2.

$$n\lambda = 2d \sin \theta \quad (3.2)$$

Where n is an integer, λ is the wavelength of the X-ray beam, d is the spacing between crystal planes, and θ is the angle of scattering [109]. Bragg's Law is also known as the diffraction condition for constructive interference. The condition is that the length of the path difference between the X-rays reflected from one layer and the next, is an integer multiple of the wavelength of the X-ray beam [109, 110]. When this condition is satisfied, the scattering of the X-rays produce a characteristic diffraction pattern. This condition is only satisfied when $\lambda \leq 2d$ [110]. Each crystalline material possesses a characteristic XRD pattern, therefore XRD may be used to identify crystals. It may also be used to distinguish between amorphous and crystalline materials [109]. The diffractometer which is used for XRD analysis, is constructed so that the sample rotates in the path of the collimated beam of X-rays at an angle of θ . The X-ray detector is mounted on an arm to enable the diffracted X-rays to be detected at an angle of 2θ [110]. For XRD analysis, data is typically collected over a range of $5^\circ - 70^\circ$ for 2θ .

The XRD pattern for graphite exhibits a characteristic peak around $2\theta \approx 26^\circ$. This corresponds to an interlayer spacing of 0.34 nm [102, 111]. This peak is the (002) peak and is an indication of crystallinity [112]. Wang *et al.* [113] showed that this peak gradually decreases in intensity while the GO peak at approximately $2\theta \approx 11^\circ$ increases in intensity as the oxidation of the graphite progresses until the graphite peak eventually disappears. Therefore, XRD analysis may be used to monitor the level of oxidation of graphite into GO. As mentioned, the XRD pattern for GO displays a defined peak at $2\theta \approx 11^\circ$ which corresponds to an interlayer spacing of 0.76 nm [111]. The XRD patterns for both graphite and GO can be seen in Figure 3-18. The

interlayer spacing of GO varies proportionally to the level of oxidation [12] as a larger distance between layers of GO is a direct result of the introduction of various functional groups during the chemical oxidation process [102, 113].

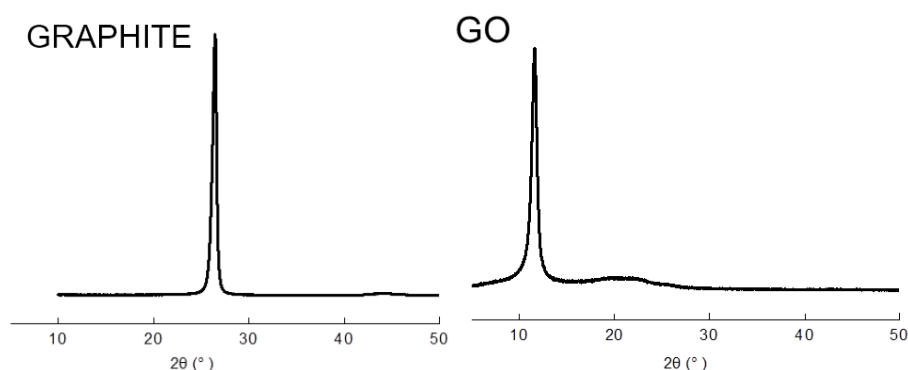


Figure 3-18 XRD patterns for graphite and graphene oxide (GO) [111].

Following the chemical reduction of GO to form graphene, the crystalline structure of the original material in 2D is restored. Proof of this is in the restoration of the (002) diffraction peak and the disappearance of the characteristic GO peak [113]. The absence of this GO peak upon reduction shows that the interlayer spacing has decreased significantly [107]. Figure 3-19 depicts the XRD pattern for graphene which has been attained via the chemical reduction of GO. This material exhibits a characteristic peak which approaches that of graphite but may be found between $2\theta \approx 24^\circ - 26^\circ$. The value of 2θ varies proportionally to the number of graphene layers [112] which is depicted in Figure 3-20. Although this peak may lie close to that of graphite, the intensity of the graphene peak relays information about the number of layers and thickness of the graphene present which makes it possible to distinguish graphene from graphite [112]. While single- and bi-layer graphene do not exhibit a definite XRD peak, three-layer graphene exhibits a low intensity, broad peak located at $2\theta \approx 24.3^\circ$. This peak narrows and increases in intensity as the number of layers of graphene increase [112]. Therefore if no XRD peak is present, this implies that the graphene is single- or bi-layer or exhibits a non-crystalline structure [112]. It should be noted that as the number of layers of graphene approaches 10 layers, the XRD peak of the material becomes more similar to that of graphite; this is consistent with the expected behaviour of graphene as this 10-layer limit is approached.

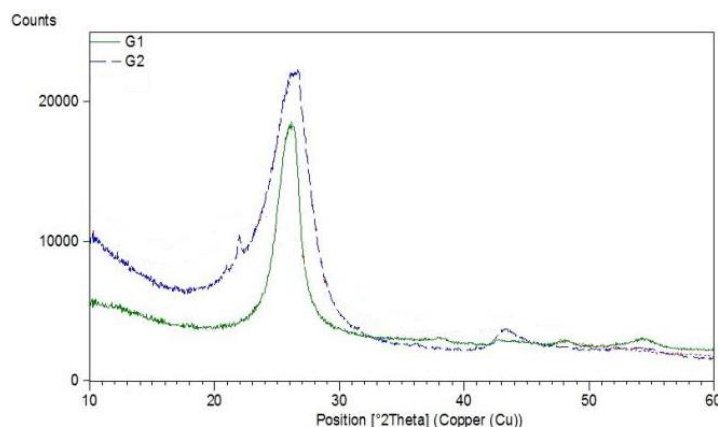


Figure 3-19 XRD pattern of chemically reduced graphene samples [107].

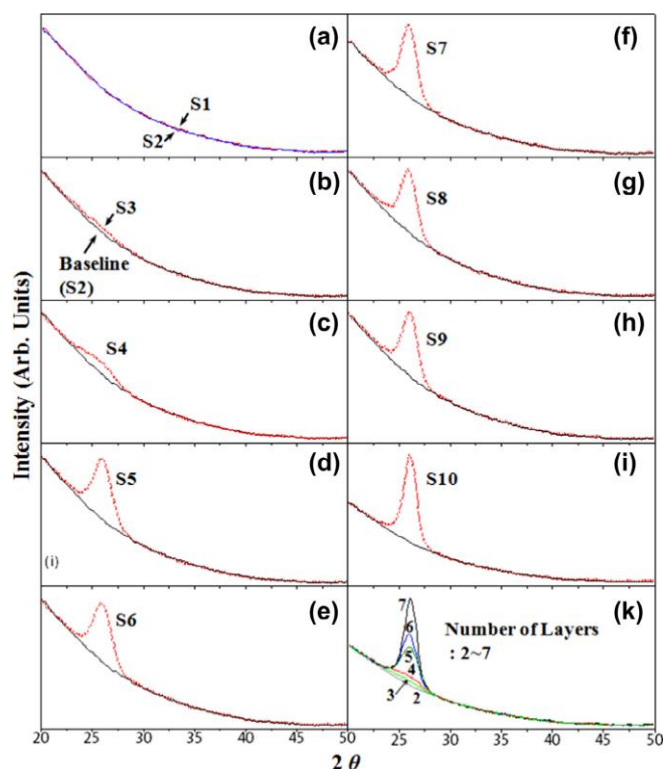


Figure 3-20 (a - i) XRD patterns for graphene where the numeric value indicates the number of layers, (k) the combined XRD plot for all the graphene samples [112].

3.5. Degradation of graphene and graphene oxide

It is of the utmost importance to investigate the chemical stability of graphene prior to its implementation in any application so as to ensure that the various devices in which it is integrated can provide a long-term performance and safety. Due to the infancy of graphene technology, thorough investigation of its degradation through interaction with biological and environmental elements has not yet been undertaken [114]. It is possible that graphene-related technology may become commercially available in the near future, therefore this has triggered a number of studies on its interaction with humans and the environment, as well as its effects on them [115-118].

Furthermore, a number of biomedical uses have been suggested for graphene. Therefore, it is necessary to assess its interaction with humans prior to its incorporation into such technology.

A study which investigated the oxidative degeneration of carbon nanotubes has been replicated in order to study the same process in graphene. This research examined the oxidative degeneration of pristine, multi-layer graphene using hydrogen peroxide, H_2O_2 [119]. H_2O_2 is an oxidising agent and is found in minute concentrations in several natural sources including rain water and other sources of water ($1 - 7 \times 10^{-3}$ M [120]) as well as in living cells ($1 \times 10^{-9} - 700 \times 10^{-9}$ M [120]). Oxidative stress occurs when the concentration of H_2O_2 exceeds 1×10^{-6} M [121] therefore even these minute quantities of H_2O_2 pose an oxidation risk and thus must be investigated. Xing *et al.* [114] found that pristine multi-layered graphene submerged in various concentrations of H_2O_2 developed holes after a few hours due to the oxidising nature of the H_2O_2 . The H_2O_2 broke down the carbon-carbon bonds of the graphene. This effect was aggravated by increasing concentrations of H_2O_2 . The findings of their study revealed that the concentration of H_2O_2 found in naturally occurring sources causes degradation of graphene [114]. In addition, graphene synthesised via CVD may have residual amounts of nickel present and this may serve to further accelerate this degradation [114].

Other studies on carbon nanotubes may be tentatively applied to graphene while further studies are underway. Research has been conducted on the effects of various enzymes found in the human body as well as in the bodies of other animals on carbon nanotubes and the conclusion of these studies was that degradation of the carbon nanotubes could be exacerbated by these enzymes in an H_2O_2 environment [114]. The degradation was only effective when the samples were continuously subjected to oxidative stress by the enzymes and H_2O_2 . And while these enzymes are restricted to living cells, H_2O_2 is an environmental oxidising agent and therefore its effect on the degradation process is more relevant. However, Xing *et al.* [114] acknowledged that further research needs to be conducted since their findings were limited in that the controlled environment allowed all the H_2O_2 present to react with the graphene samples while in nature there are other redox reactions which would hinder or accelerate the degradation process.

In order for graphene to be incorporated into electronic devices, it must be supported on a suitable substrate such as glass, silicon dioxide quartz (SiO_2) as well as other oxides [122]. Unfortunately, the disadvantage of these oxide substrates is that they serve to reduce single-layer graphene's resilience against oxidation [123-126]. An investigation of the degradation of single-layer graphene on SiO_2 in particular was carried out by Roy *et al.* [122]. It was found that the substrate has adverse effects on the oxidation of single-layer graphene under ambient conditions. It was also found that the presence of water vapour accelerates the degradation process [122]. This may be caused by the presence of H_2O_2 in the water vapour, therefore the resilience of graphene on a substrate such as SiO_2 can be improved by reducing its exposure to humid air [122].

In addition, Yamamoto *et al.* [125] showed that single-layer graphene displays less resistance to oxidation than multi-layer graphene.

Another consideration is the degradation of graphene derivatives such as GO. It is necessary to consider the degradation of GO since the proposed method of synthesising graphene involves the chemical reduction of GO. GO degrades by enzymatic action in the presence of H₂O₂ [4]. Enzymes responsible for this degradation are, for example, horseradish peroxidase, myeloperoxidase and eosinophil peroxidase [4, 127] which can be found in horseradish herb [128], white blood cells [129, 130], and granulocytes, respectively [131]. However, reduced GO, which is considered graphene, is more resilient against degradation by these enzymes.

3.6. Applications

The applications of graphene are numerous and rapidly expanding into a variety of fields. This is evident in the number of graphene-related patents published in recent years. According to the U.K. Intellectual Property Office, in 2011 the number of graphene-related patents totalled 3 018 and by 2015, that number had escalated to 25 885 [132]. The patents cover a wide range of applications, ranging from electronics to medical and energy applications. In fact, the applications of graphene are so vast that the British government has funded a National Graphene Institute which was completed earlier last year (2015), and the European Union funded Graphene Flagship initiative was launched in 2013 [8]. This initiative is especially significant since it comprises a consortium which spans 23 countries and includes 142 academics and industrial researchers whose primary objective is to develop graphene from a material of purely academic interest into commercial technology within 10 years [8].

Since graphene is considered “unzipped” carbon nanotubes, many of the applications of carbon nanotubes could relate to graphene as well [17]. The various exceptional and unique properties of graphene allow for its application in a number of fields, and therefore the graphene itself could be optimized for a specific use which exploits only certain properties. A selection of applications of graphene are elaborated upon in this section.

Energy-related applications

Graphene’s exceptional thermal and electrical conductivity make it potentially suitable for utilisation in several energy-related applications including, but not limited to, fibrous wires, batteries, supercapacitors and solar cells [4]. As mentioned previously in Section 3.2.3, ballistic transport occurs at room temperature in the range of mere micrometres [21]. This implies reduced electrical resistance since the electrons travel without scattering [34] which in turn results in the potential for great energy-loss reductions. While graphene may not exhibit conductive properties within the league of superconductors, its primary advantage over superconductors is that it offers

low resistivity at room temperatures and this would eliminate the cost of cooling of the superconducting materials.

Graphene fibres

The application of interest in this dissertation is graphene fibre. While graphene fibres have been previously fabricated, this research aims to produce graphene fibre using an alternative method, i.e. via electrospinning using a carrier polymer, in this case polyvinyl alcohol (PVA). The appeal of graphene fibre is that it potentially integrates the exceptional characteristics of graphene with that of conventional fibres to produce a material which exhibits a combination of these properties. The prospective applications of such fibre include conductive wire, photovoltaic cells and supercapacitors [5]. This section serves to present some of the current, known methods of producing graphene fibres.

While carbon-based fibres have been successfully produced through the use of carbon nanotubes which resulted in fibres characterised by high mechanical strength and high thermal and electrical conductivities [5], the primary reason behind the desire to fabricate fibres from graphene is to exploit the superior properties of this 2D material. In addition, a lower cost is incurred during the production of graphene-based fibres when compared to their carbon nanotube and carbon fibre counterparts [5]. Graphene fibres have been shown to outperform copper wires in terms of thermal conductivity [133]. Furthermore, the long-range crystalline order of graphene renders the effects of grain boundaries in the lateral direction almost null. In this way, graphene fibres may surpass the restrictions of existing carbon fibres [134]. However, the boundaries between the graphene flakes themselves may impose limitations on the graphene fibre.

Graphene fibres were produced by Xu *et al.* [135] through the chemical reduction of GO fibres. GO is commonly used to produce graphene fibres since it readily disperses in a suitable solvent and can therefore easily be spun into fibres [41]. The process as reported in [135] is as follows: GO solutions were prepared and injected into a sodium hydroxide/methanol bath which caused the fibres to coagulate. The solubility of GO in water allowed it to form what is known as lyotropic nematic liquid crystals. These are mixtures of amphiphilic molecules and a solvent which displays long-range orientational order [135, 136]. This property of GO allows the aqueous GO to be wet-spun into fibres by loading the solution into a glass syringe and injecting it into a coagulation bath [135]. The fibres were then reduced using hydroiodic acid to form graphene fibres. This process is highly scalable and the fibres produced were flexible, however they lacked mechanical strength [135]. Cong *et al.* [137] also produced graphene fibres using a similar method which is known as the wet-spinning of GO solutions followed by the chemical reduction of these fibres. The fibres resulting from this process were macroscopic (diameters of 50 – 100 μm) and contained multiple functional groups. However, these fibres also exhibited a low tensile modulus [5] thereby indicating that these fibres cannot be draw out to any significant length without

causing breakage. Xiang *et al.* [41] addressed this drawback by using GO flakes with an average diameter of 22 μm . This resulted in fibres with a tensile modulus that was far higher than those reported above. The research by Xiang *et al.* [41] investigated the effect of the GO flake size on the overall performance of the resulting fibres rather than the formation of graphene fibres. However, this research still has relevance here since the fibres produced using this method may be chemically reduced to produce graphene fibres. The GO fibres were formed via the extrusion of a GO suspension directly into an ethyl acetate coagulation bath [41]. The GO fibres made from larger flakes of GO ($\sim 22 \mu\text{m}$) exhibited a 100% knot efficiency[†] which is a measure of fibre stress. No polymer fibre has exhibited a knot efficiency of this magnitude [41]. This behaviour can be attributed to the low bending modulus of single-layer graphene itself which implies that it is a highly flexible material [138, 139]. GO fibres produced using smaller flakes ($\sim 9 \mu\text{m}$) did not exhibit this behaviour, however, these fibres appeared to be far more aligned due to the alignment of the liquid crystals of the smaller GO flakes themselves [41]. This property of GO has been discussed above.

The wet spinning of GO is the most common approach towards obtaining graphene fibres, however alternative methods do exist. One such method is via the hydrothermal treatment of GO whereby GO solutions are sealed within a pipeline and subjected to a hydrothermal stage and are later extruded and annealed [134]. The hydrothermal stage involves the heating of the GO aqueous solution at 230 °C for 2 hours within a glass pipeline [140]. The hydrothermal stage of the process results in the spontaneous formation of graphene sheets. Another method was presented by Li *et al.* [141] which involved the production of graphene fibres through the chemical reduction-induced self-assembly of GO dispersions. This method appears to be the simplest of these methods. The process is as follows: the GO dispersion was injected into a pipeline together with the reducing agent, which was ascorbic acid (vitamin C), and heated to 80 °C for an hour. This resulted in the formation of a graphene fibre which was dried overnight. The fibres produced using this method were conductive and exhibited mechanical and tensile strength [141]. Additional methods to produce graphene fibres over and above those presented here are currently employed, however, only those which may be implemented in the Materials Science Laboratory have been detailed in this dissertation.

The various routes towards to the reduction of GO fibres to obtain graphene fibres result in the following conductive properties for different reducing agents: $2.85 \times 10^4 \text{ S.m}^{-1}$ for thermal reduction [142], $8.1 \times 10^3 \text{ S.m}^{-1}$ for ascorbic acid (vitamin C) and $2.8 \times 10^4 \text{ S.m}^{-1}$ for hydroiodic acid [143]. The conductivities for the graphene fibres produced via the aforementioned methods are far lower than that of single-layer graphene. But, a trade-off must be made between

[†] Knot efficiency is a measure of fibre stress and is calculated by dividing the breaking stress of the knotted fibre by the breaking stress of a specific control fibre [41].

the electrical and mechanical properties of the fibres since the graphene sheets are required to be highly aligned for superior electrical properties while this alignment would restrict the mechanical strength of the fibre [133]. Therefore, it is clear that the graphene fibre production process must be optimised for the specific application. Although, Xu *et al.* [143] showed that the conductivity of the graphene fibres can be significantly improved ($9.3 \times 10^4 \text{ S.m}^{-1}$) by doping the fibres using silver to form fibres which are highly conductive with high mechanical and tensile strength as well.

Supercapacitors

Graphene may be used in the form of reduced thin GO films for the production of supercapacitors. Supercapacitors are essentially electric double layer capacitors [144] and the performance of these devices, in terms of capacitance as well as energy and power density, is defined by the high surface area of the material from which the electrodes are fabricated in addition to the extremely small separation of charges [4]. The electrodes of supercapacitors are typically produced using a material which offers high conductivity and surface area [144]. Graphene appears to be a potentially suitable material for the production of more efficient supercapacitors since it is an intrinsically thin, flexible material and therefore the electrodes fabricated using this material would be thinner and provide a larger surface area thereby increasing the energy density and, in turn, the efficiency of the device compared to conventional devices [4]. Furthermore, this material possesses properties such as chemical stability, high electrical conductivity as well as mechanical strength which render it potentially ideal for the production of supercapacitors [144].

Zhang *et al.* [51] prepared thin films of activated, reduced GO which were used as the electrodes of supercapacitors. The resulting equivalent resistance of these electrodes ($\sim 0.1 \Omega$) proved to be marginally less than that of electrodes fabricated from carbon nanotubes, however, the power density of the graphene electrodes as reported by Le *et al.* [144] was significantly lower than that of their carbon nanotube counterparts. The reduced GO films were activated using potassium hydroxide which resulted in films that were highly porous and conductive as well as flexible with a large-surface area [9]. Films with these properties may also find use in lithium-ion batteries in addition to forming conductive substrates for various composites [9].

Solar cells

The electrical and optical properties of graphene may be exploited to produce highly efficient solar cells [145]. Photovoltaic cells are optoelectronic devices of which one of the defining components is the electrode which is required to be transparent and conductive [146]. The electrode is often made using indium tin oxide (ITO) due to the low resistivity of this material. However, ITO is a rare and brittle material which results in an expensive and relatively fragile

product [51]. Graphene films present an alternative to indium tin oxide and offer similar properties such as optical transparency and high conductivity which provide the potential for the production of efficient solar cells with the added benefit of flexibility as well as better cost-efficiency [13]. Zhang *et al.* [51] showed that the anode of photovoltaic cells fabricated through the use of Chemical Vapour Deposition grown graphene produced an output power density which was 93 % of their indium tin oxide counterparts. This is impressive considering that the graphene films have a far higher sheet resistance and are less transparent than the indium tin oxide cells. This apparent difference in resistance can most likely be attributed to the functional groups failing to be completely removed during the reduction of the GO films [146]. While graphene may fall short in these two areas, it does offer the additional advantage of flexibility which is lacking in indium tin oxide. This property allows the graphene films to be bent without the formation of cracks in the film which would increase its resistivity [51]. The advantage is that flexible cells could be produced without compromising the conductive properties of the material.

Transistors and electronic components

The application of greatest significance is possibly the potential for graphene as a substitute for silicon. It is widely acknowledged that the existing silicon-based technology is rapidly reaching its fundamental limits [10, 36]. Therefore, the potential for a possible substitute such as graphene is extremely significant. In fact, IBM and Intel are actively funding graphene research [10]. This highlights the very real possibility of graphene's application in transistor technology. Graphene possesses a number of superior electronic properties when compared with silicon which makes it suitable for possible applications in electronic devices in the nanoscale; these properties include its extremely high charge carrier concentrations as well as high mobilities [11].

The high mobility of charge carriers in graphene is the property which makes it a potentially ideal candidate for high-frequency electronic applications [13], transistor technology in particular [36]. The charge carrier mobility of graphene is significant since even electric field induced concentrations do not hinder this exceptionally high mobility of the charge carriers [10]. As mentioned previously, this implies ballistic transport occurs at room temperature in the range of mere micrometres [21] which enables the possible production of ballistic transistors capable of operating at room temperature [10].

The one hindrance to the development of graphene transistors is its lack of a bandgap since single-layer graphene exhibits semi-metallic behaviour [10]. As a result, field-effect transistors fabricated from graphene have low on/off ratios [10] which in turn results in power losses [4]. In order for graphene to be processed into transistor devices, the intrinsic zero-bandgap of the material needs to be modified without adversely affecting its other electronic properties. To address this obstacle, the material may be chemically modified through hydrogenation to induce a non-zero bandgap. Examples of such materials are graphane and fluorographene [4]. This may

also be achieved by substitutional doping using nitrogen to potentially create a p-type semiconductor [147]. An alternative approach to opening the bandgap of graphene is through the epitaxial growth of graphene on a suitable substrate. This method has proved successful through the use of hexagonal boron nitride [148], silicon dioxide [149] and silicon carbide [150] as substrates.

In addition to applications in the transistor industry, graphene's other exceptional characteristics may be exploited which may find applications within the mobile technology industry as well. Graphene is a flexible, transparent, strong conductor thereby rendering it potentially useful in the production of flexible touchscreens and electronic components for smart devices, and it would be cheaper as well as stronger than currently utilised materials such as indium tin oxide [13]. The flexibility of graphene enables the potential production of wearable electronics which can safely interact with the human body [4].

Composite materials

Due to graphene's superior strength characteristics, it may be used as a strengthening filler in many composite materials such as polymers and building materials [6]. Graphene's superior mechanical strength has already been discussed, therefore it shall not be reiterated here except to highlight that graphene has been found to possess an extremely high specific strength which is higher than that of any other presently known material [19]. This property makes it a suitable material for strength related applications where the graphene layer could act as the load bearing material [6]. While the application of graphene in the electronic industry may only become a reality in future years, this particular application of graphene in composite materials may be realised presently. The benefit of the addition of graphene would be that the resulting material could be engineered to become conductive, if so desired [151]. Various studies have shown that even low volumes of graphene when added to a material such as a polymer matrix results in greater thermal and electrical conductivity and an increase in the Young's modulus of the material [151-154]. In addition, the high strength-to-weight ratio of graphene renders it appealing for use in satellites, aircraft and even motor vehicles where it could reduce the mass of the vehicle and thereby reduce fuel consumption [13].

In addition to its strength properties, graphene is an unreactive material when exposed to ambient conditions and can therefore be used as protection against corrosion [155-158]. Since graphene may be grown on many metal substrates and is hydrophobic [4], it could be employed to act as a surface coating against rust and thereby protect the underlying metal. Graphene achieves this by preventing the oxidation of the metal as well as the reduction of oxygen [156]. Graphene may be employed in the form of reduced GO which is also very effective in the prevention of corrosion of the underlying metal. The advantage of this is that the reduced GO can

be used in its multilayer form with the same effect, and this form of graphene is simple and inexpensive to produce [157].

Water purification applications

Toxic chemicals are becoming more prevalent in natural sources of water due to industrial activities, however, existing methods of removing pollutants such as arsenic are costly [7]. It is imperative that arsenic be effectively removed from these water sources since it is toxic to both animals and humans [7]. Graphene poses a solution to this problem. Mishra *et al.* [7] showed that functionalized sheets of graphene may be used to remove arsenic from water sources as well as to desalinate sea water. Graphene oxide films prepared via the Hummers' method were exfoliated at 200 °C in a hydrogen atmosphere which led to the formation of graphene sheets. These graphene sheets were then functionalized via treatment with nitric acid and processed into electrodes for use in a supercapacitor filter for water. The supercapacitor was used to filter contaminated water by applying a voltage to the electrodes of the supercapacitor which resulted in the adsorption of the arsenic and sodium [7].

Another study made use of porous graphene membranes for the desalination of sea water via reverse osmosis. While other reverse osmosis membranes are currently used for desalination, graphene is potentially superior in terms of film thickness, very high mechanical strength and the possibility of employing a greater variety of operating conditions [159]. Chemically functionalized graphene may be tuned so as to be used to filter salt from water. This can be achieved through the use of a graphene membrane having a pore size in the nanometer range which permits the flow of water through it but prohibits the flow of salt ions across it [159].

In a water scarce country such as South Africa, a cost-effective method for the desalination of sea water is immensely useful. The current drought situation along the east coast and further inland has had a crippling effect on many farms. This fresh water could be used to provide relief to famers and thereby reduce food prices. Although this particular application is not the focus of this dissertation, it deserves specific mention due to its immediate relevance.

Graphene oxide applications

GO may be deposited onto a suitable substrate to form thin films. These films can then be reduced which results in flexible and optically transparent devices [45]. Single-layer and few-layer reduced GO films exhibit graphene-like, semiconducting behaviour whereas multi-layer films exhibit behaviour similar to that of graphite [45]. Eda *et al.* [45] used the vacuum filtration method to uniformly deposit a GO suspension on a filter membrane to form thin films which can then be transferred on to a suitable substrate. The films are reduced using hydrazine vapour followed by annealing in a vacuum furnace [36, 63, 65, 76, 89, 160-162] to form the electrically conductive graphene. The lowest achieved sheet resistance for the films fabricated via the

aforementioned method was $43 \text{ k}\Omega \cdot \text{cm}^{-1}$ [45]. These films may be further developed for use in transistors and photovoltaic cells.

Furthermore, GO may be used for the removal of radioactive waste in solution. GO in particular is potentially suitable for environmental applications since it is a non-toxic as well as biodegradable material [12, 163-166]. The various functional groups which can be found on the surface of GO interact with ionic particles and can aid in the removal of nuclear waste in solution [167]. Research conducted by Romanchuk *et al.* [167] showed that when nuclear waste is added to a solution of GO in water, the waste causes the GO to coagulate. While GO is intrinsically hydrophilic and readily disperses in water, the precipitate that forms consists of the GO particles together with the nuclear waste particles. The nuclear-waste-containing precipitate can then be filtered and the solution is purified. This method of removal of nuclear contaminants provides a simple and low-cost approach [167] using the material GO which can be synthesised in large volumes using traditional, low cost methods such as the modified Hummers' method.

3.7. Summary

A comparison of the energy band structure of single-, bi- and few-layer graphene showed the exceptional properties of graphene are only observed in single-layer pristine graphene. However, the Fermi level of graphene may be altered through the application of an electric field or via adsorption of water or ammonia. This alters the electrical conductivity of graphene making it potentially higher than that of copper [13]. Graphene's superior electronic and mechanical properties justify its consideration in the application of interest in this research: graphene processed in the form of graphene fibres for various applications. While there are many applications for this material, it remains difficult to isolate graphene in its pure, pristine form. However, the study of graphene is yet in its infancy and great potential exists in this field of materials science.

Although the chemical exfoliation of graphite to produce graphene introduces defects into the graphene oxide in the form of functional groups, most of these defects are removed during the chemical reduction process. And while the conductivity of graphene produced via this route is lower than that produced via mechanical exfoliation, the chemical exfoliation process offers a method that is scalable and cost-effective which is suitable for the application of interest in this dissertation as well as for the production of graphene in the Materials Science Laboratory.

Chapter 4 Electrospinning

The primary objective of this research was to produce graphene via various routes for the fabrication of graphene fibres. The adopted approach was to electrospin graphene flakes suspended in a polymer solution to generate graphene fibres. Electrospinning has previously been used in an attempt to enhance the mechanical and electrical properties of electrospun polymer fibres by adding carbon nanotubes. It was found that the presence of carbon nanotubes led to an increase in the conductivity of the fibres and improved the fibres' electrical characteristics such as the electromagnetic shielding and electrostatic charge dissipation [168]. Since conductive fibres were successfully obtained through the electrospinning of carbon fibre and polymer into composites, it was decided for this project to attempt to extend this to graphene to produce graphene and polymer composite nanofibres. The premise was that the graphene present in these fibres will potentially increase the conductivity and mechanical strength of the material so that it may be used in various applications.

The following chapter comprises a review on the electrospinning process. This includes a brief history of electrospinning, a description of the process itself, the various solution, processing and ambient parameters involved, and existing methods used to characterize nanofibres made from various materials. The chapter concludes with select applications of electrospun graphene and polymer composite fibres.

4.1. The electrospinning process

Electrospinning is a technique that is used to fabricate fibres through the use of a high strength electric field. The fibres produced are typically polymer fibres with diameters in the range of 2 nm to a few micrometres [169]. Electrospinning techniques were employed in the earlier part of last century by the textile industry for producing non-woven fabrics [169]. This process has been revisited in recent times due to the simple, inexpensive and efficient method it offers to produce nanofibres [170]. Electrospinning has gained significant attention owing to its capability of fabricating fibres in the nanometric range which has proved difficult using other, existing mechanical fibre fabrication methods [171-174]. Electrospun fibres offer a number of advantages

including: smaller pores and higher surface area than other fibres, very high surface-to-volume ratio, flexibility to be moulded into various sizes and shapes, superior mechanical performance [170], and the opportunity to tune the fibre composition to meet the requirements of the user [169]. These desirable characteristics of electrospun nanofibres lead to their application in several fields, such as tissue engineering, biomedicine, pharmacy, opto-electronics, biotechnology and environmental engineering [175-181]. Furthermore, electrospinning offers a low cost method of producing these nanofibres [169] which may be fabricated from various materials. As mentioned, other nanofibre fabrication techniques exist, such as phase separation and template synthesis, however very few of these methods can equal the versatility, flexibility and simplicity offered by the electrospinning process [182]. This process is typically used to produce polymer fibres however it has also been used to produce composite, semiconducting and ceramic nanofibres [172, 183, 184]. The fibres produced via electrospinning may also be functionalized by adding various nanoparticles, including drugs, catalysts and semiconductor nanoparticles [185].

The electrospinning process itself is based on the fact that fine fibres can be drawn from solution through the aid of a strong electric field using a conducting spinneret [186]. The apparatus used for electrospinning comprises three primary elements, namely: the spinneret used for dispensing the solution, the high voltage DC power supply and the conductive collector plate. The first step of the process involves dissolving a polymer in a suitable solvent and loading this solution into a syringe with an attached conductive spinneret such as a needle which acts as an electrode [185]. For electrospinning solutions that typically give off harmful odours, the process should be executed in an enclosure equipped with a ventilation system [172]. The syringe is usually mounted onto a syringe pump for consistent, controllable dispensing of the solution [170]. A high voltage DC power supply is usually connected to the spinneret thereby applying a voltage of > 5 kV to the solution [182] while the collector is grounded. However, the reverse configuration may also be used [169]. The solution is dispensed through the spinneret and is held at the end of the needle by its own surface tension. An electric charge is induced on the surface of this solution due to the applied high voltage [169] which creates an electric field between the spinneret and the grounded collector. The applied voltage is slowly increased until it reaches a critical value at which the induced repulsive forces exceed the surface tension forces of the solution resulting in the formation of what is known as a Taylor cone [169]. An illustration of this Taylor cone is shown in Figure 4-1. Once the applied electric field surpasses this critical point, a charged jet of solution is expelled from the end of the Taylor cone. This jet is stable just beyond the end of the spinneret due to mechanical causes [186]. However, it soon becomes unstable leading to a whipping motion of the jet [169, 182]. This motion leads to the evaporation of the solvent and the drawing of the electrospinning jet thereby resulting in the deposition of a polymer fibre on the collector [169, 170].

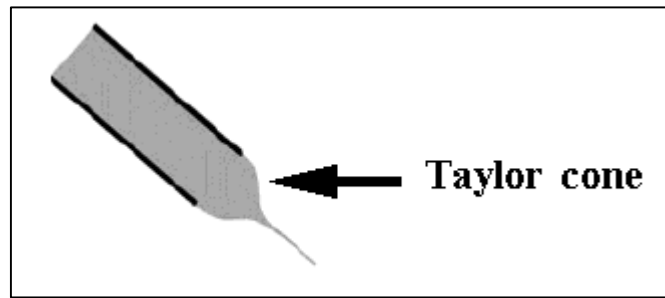


Figure 4-1 Taylor cone formation at the end of the spinneret [170].

4.2. The electrospinning apparatus

A schematic of the electrospinning apparatus is depicted in Figure 4-2. This apparatus may be arranged in two standard configurations: the vertical and horizontal configurations [169]. Fibres have been observed to be deposited randomly in the vertical configuration due to bending instability of the electrospinning jet [187]. The disadvantage of the vertical configuration is that if the electrospinning parameters have not been optimised this configuration could result in the solution falling onto the collector before being spun into fibres thereby making the collection of the fibres difficult. When the horizontal configuration is used, the induced electric field is parallel to the floor resulting in a higher voltage being needed. The electrospun fibres follow a projectile motion and therefore these fibres are generally deposited towards the bottom of the collector plate [187]. The advantage of the horizontal configuration is the aforementioned problem potentially experienced with the vertical configuration will be avoided using this configuration and the fibres will not be interspersed with the solvent on the collector. This allows for easier collection of the electrospun fibres.

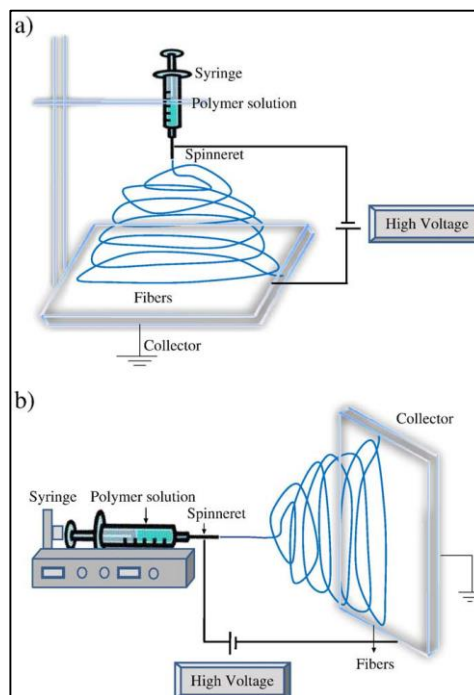


Figure 4-2 Diagram of the two basic configurations of the electrospinning apparatus, a) vertical and b) horizontal [169].

4.3. Polymers used for electrospinning

Various materials may be used for electrospinning although nanofibres are most commonly fabricated from polymer materials [169]. Two such polymers which shall briefly be elaborated upon here are polyvinyl alcohol (PVA) and polystyrene. When polymers, in particular, are electrospun, the fibre diameters approach the nanometer scale and exhibit many advantageous properties over other forms of the same material [172]. These properties include an exceptionally high surface-area-to-volume ratio, a large degree of flexibility and improved mechanical strength [172]. Due to these properties, electrospun polymer fibres are suitable for a number of potential applications which shall be discussed later in this chapter.

4.1.1. Polyvinyl alcohol (PVA)

One of the most commonly electrospun polymers is PVA because it is easily processed, it is biocompatible, and it is non-toxic as well as hydrophilic [188-190]. Due to these highly attractive properties of PVA, it is used in a number of commercial applications which include membranes, adhesives and various coatings [191]. On the other hand, due to its hydrophilic nature, PVA's applications are limited and to non-aqueous environments as the material would dissolve in water [191]. PVA is chemically stable under ambient conditions [192] and does not react with the graphene thus making it a suitable polymer material for the electrospinning of graphene/PVA composite fibres [193]. The concentrations of the PVA solutions used for electrospinning are usually between 6 % (wt.) and 8 % (wt.) [192, 193]. PVA may be used in two forms which are classified based on the degree of hydrolysis: partially hydrolysed PVA and fully hydrolysed PVA [192]. The degree of hydrolysis of PVA influences its solubility in water. The solubility of fully hydrolysed PVA (99%) can be compared to a step function: it does not easily dissolve below 70 °C however it readily dissolves in water above 70 °C [194] forming a clear, homogenous solution in less than an hour [191].

4.1.2. Polystyrene

Polystyrene is another polymer which is commonly used in electrospinning as well as in the production of various thermoplastic materials as it possesses favourable properties such as stiffness, gloss, optical transparency and high resistivity [195, 196]. This polymer can be dissolved at room temperature in a number of solvents, including dimethylformamide (DMF), ethyl acetate, amyl acetate and tetrahydrofuran (THF) [197, 198]. The concentrations of polystyrene solutions used for electrospinning are usually between 10 % (wt. /vol.) and 30 % (wt. /vol.) [195-197]. The nanofibres produced using polystyrene may be used in several fields, including composite materials [199], sensors [200] and tissue engineering [201].

The disadvantages of this polymer are that the polystyrene requires several hours to three days to dissolve completely in the solvents mentioned in order to form a homogenous, clear solution suitable for electrospinning [197]. Additionally, these solvents, DMF and amyl acetate in particular, can cause respiratory discomfort [82, 202], which is why for this project, PVA was chosen as the polymer to be used for electrospinning.

4.4. Electrospinning solution parameters

The electrospinning parameters are influenced by the nature of the polymer itself and include molecular weight, concentration, viscosity, surface tension, and conductivity of the electrospinning solution [169]. The concentration and viscosity are interdependent since an increase in the polymer concentration of the solution will lead to a corresponding increase of the viscosity of the solution [203] therefore these parameters shall be discussed together.

The molecular weight of the polymer is a factor which is determined by the solute (polymer material) and influences the solution's viscosity, surface tension and conductivity since it is a measure of the degree of chain interactions within the polymer solution [169]. Polymers of higher molecular weights are usually chosen for electrospinning as this results in solution viscosities which are within the acceptable range for electrospinning while polymers with low molecular weights produce fibres with a high degree of beading [169]. Beading is the formation of large drop-like deposits on the electrospun fibres. Gupta *et al.* [204] found that less beading and fewer unspun droplets are formed for polymers of higher molecular weights.

The concentration of the electrospinning solution also determines the viscosity of the solution as the viscosity is directly proportional to the concentration of the solution. The concentration of the polymer solution itself determines the uniformity of the fibre. At low concentrations the fibres appear beaded and non-uniform, but at higher concentrations, this beading is not present, and largely uniform nanofibres are observed [192, 195, 205] due to the fact that chain entanglements within the solution are only formed when there is an adequate amount of polymer present in solution [206, 207]. On the other hand, if the concentration of the solution is increased to the point where the viscosity of the solution becomes very high, it will be impossible to electrospin the solution due to difficulties in dispensing such a solution [207] and due to the magnitude of the electric field which would be required to overcome the surface tension of this solution [206]. Therefore, there lies an optimal range for the solution concentration where electrospinning will be successful. The solution concentration also affects the diameter of the fibres. An increase in the concentration of the polymer solution results in fibres with larger diameters [187, 192].

Surface tension is also influenced by the nature of the solvent chosen in which to dissolve the polymer, and this parameter also influences the morphology of the spun fibres [169]. It was

found that solutions with lower surface tension produced nanofibres with little or no beading since higher surface tensions require greater electrostatic forces in order for the Taylor cone to be formed and for electrospinning to begin. Therefore the resulting jet is unstable and non-uniform fibres are produced [169]. However, the surface tension is also determined by the concentration of the polymer material present in solution. If this concentration is too low, the solution will be unsuitable for electrospinning due to an insufficient surface tension of the solution [206].

The conductivity of the solution depends on the polymer material as well as the solvent used since this determines the number of charged ions present in solution [169]. Solutions with more charged ions have a higher charge carrying capacity [206]. Solutions with very high conductivities result in unstable electrospinning jets when exposed to the electric field. This results in a higher degree of bending instability and thus fibres with great variations in diameter [169, 206]. However, it has been reported that solutions that are highly conductive produce far narrower electrospun fibres [208] while solutions with very low conductivities result in beaded electrospun fibres [169]. The conductivity of the electrospinning solution may be altered by introducing various ionic salts which provide more charged ions in solution. It has been shown that more uniform fibres with less beading have been produced using this method [192, 209].

An additional solution parameter is the degree of hydrolysis of the solute. Zhang *et al.* [192] showed that when PVA with a high degree of hydrolysis was used, the tip-to-collector distance does not appear to affect the morphology of the electrospun fibres. In addition, the hydrolysis of the precursor polymer affects the morphology of the fibres where PVA of a higher degree of hydrolysis resulted in more uniform fibres [192].

4.5. Electrospinning processing parameters

The electrospinning processing parameters entail those factors involved in the electrospinning procedure which directly affect the fibre morphology and/or distribution thereof [196]. The parameters which are discussed here are: delivery system, flow rate, collection system, tip-to-collector distance and applied voltage.

4.5.1. Delivery system

The most common delivery system involves the use of a single syringe with an attached needle or a pipette as the dispensing device [169, 192, 206]. Most systems employ a single spinneret for dispensing the electrospinning solution. However, this results in a low throughput, and much research has been conducted to ascertain various possible routes to increase this throughput. Such a need arises due to the industrial requirements for large volumes of fibres for various applications [210]. One such method involves using multiple spinnerets assembled in a single line [173, 211] to dispense larger volumes of solution without compromising the other

processing parameters such as the flow rate. However, this method requires a higher applied voltage [210]. The advantage of this method, apart from the increased fibre yield, is that a fibrous mesh consisting of one or more different solutions may be formed [182]. The disadvantage of using multiple spinnerets is that the electric field is disturbed due to the presence of these additional needles. This can eventually cause the field to weaken which would in turn affect the morphology of the spun fibres [210].

Another method whereby the fibre yield is improved, is through the use of a porous electrospinning tube surrounded by a collector in the form of a cylindrical, conductive drum [182]. The electrospinning solution is filled into the tube and pushed out through the application of air pressure. The tube rotates while the solution is dispensed and is electrospun [182]. This method has been shown to significantly improve the rate at which electrospinning, and therefore fibre formation, occurs [210].

An alternative method of solution delivery is the coaxial nozzle configuration which consists of a needle of a smaller diameter that lies coaxially within a needle of a larger diameter. This permits two different solutions to be electrospun at the same time [210]. This is particularly useful when one solution is unable to be electrospun in which case, the outer coating may be removed. If hollow fibres are desired, the inner polymer may be removed instead [182].

4.5.2. Flow rate

The flow rate is the rate at which the solution to be electrospun is dispensed. This parameter has been found to significantly influence the fibre morphology as well as the area of deposition and may be accurately controlled through the use of a syringe pump [170, 206].

In a study on the effect of the flow rate on the morphology and deposition of electrospun fibres, it was observed that at higher flow rates, the size of the droplets of solution was larger and the diameters, beads and area of deposition of the resulting fibres were also similarly larger [169, 170, 203]. In addition, when the flow rate was too high, more solution was dispensed which required more time for the solvent to evaporate. However, given the high flow rate, sufficient drying time was not available, therefore the fibres collected in webs rather than in individual fibres [203]. If the apparatus is configured vertically, this could also result in unspun droplets falling upon the collector [169, 170, 212].

Conversely, the same study on the effects of flow rate observed that lower flow rates produced fibres of a higher quality since the lower rate allowed the fibre to be exposed to the electric field for a longer period of time therefore the fibre would be able to dry adequately [203, 212] and could be drawn into fibres with narrower average fibre diameters [170]. Although, if the flow rate is too low for a given electric field, the Taylor cone may be forced to recede and form within the needle. Therefore, the solution would be propelled away from the spinneret at a faster rate than it is being dispensed thus producing fibres with varying diameters [170].

Rodoplu *et al.* [187] observed that a decrease in the flow rate resulted in less prevalent beading on the fibres. However, it was also noted that if the flow rate is decreased below the point at which no beading is observed, a higher applied voltage is required. Thus, these two parameters should be adjusted simultaneously to determine the optimum point for high quality fibre formation which results from a stable Taylor cone and sufficient drying time of the electrospinning jet [170, 187]. At this optimum flow rate for a constant applied voltage, uniform fibres are produced with little variance in diameter. On the other hand, if the flow rate is far above or below the optimum point, the diameters of the fibres produced will vary greatly [170, 203].

4.5.3. Collection system

In many electrospinning experimental systems, the collector takes the form of a conductive, static, metal plate which also usually takes on the role as the ground electrode of the apparatus [182]. The type of collection device used primarily influences the fibre assemblies [182]. It has been found that the type of material from which the collector is made influences the surface charge accumulation [213]. Consequently, a highly conductive material is chosen for the collector plate in order to collect more densely deposited electrospun fibres [203]. If a non-conductive material is used, the fibres would be loosely deposited [168]. When a conductive plate is used as the collector, the fibres are deposited in a non-woven mesh [168]. Aluminium foil and copper flat plates are often used as the collector. However, there are numerous other types of collectors, which include: a rotating drum, parallel electrodes or bars and various permutations thereof [169, 182].

If highly aligned fibres are required to be produced via electrospinning, a rotating device, such as the rotating drum, is the best choice for the collector as this would produce aligned, mostly parallel, nanofibres over a large area [169, 182]. The rotating drum comprises a cylindrical drum, the rotation of which is provided and controlled by a simple DC motor [168]. Aligned fibres are obtained through the rotating motion of the collection device since the electrospun jet is deposited as the drum rotates. Therefore, it is, in effect, wound around the drum. The rotating speed of the device should be taken into consideration since once the optimum speed of rotation is achieved, the fibres have been found to align along the axis of rotation [182]. However if the speed of rotation is significantly less than this optimum speed, the fibres collect in a random distribution on the drum [214]. If the speed of rotation greatly exceeds the optimum point, the fibres may break [182, 214].

Another simple method for the collection of well aligned fibres involves the use of parallel, stationary electrodes [168]. The configuration of the electrodes is such that an air gap is formed between them which repels the electrospun fibres thereby assisting in the alignment of the fibres [168, 215]. This method also allows the number of deposited fibres to be controlled by applying a voltage of opposite polarity to that of the electrospinning jet to one electrode so that the spun

fibres collect on this electrode. The other electrode is charged with a voltage of the same polarity as the previous electrode in order to cause the opposite end of the fibre to span the air gap and deposit upon the second electrode [215]. The amount of nanofibres which are deposited can be varied by switching the polarity of the electrodes [215]. The disadvantage of this method is that the length of the deposited fibres is limited to the distance between the electrodes. This distance cannot be too large since this will cause breakage of the fibres [182].

There are numerous other types of collectors, such as conductive paper, wire mesh [169] and water bath collectors [216], however, only the most common collection systems have been discussed above.

4.5.4. Tip-to-collector distance

The tip-to-collector distance is the distance between the end of the spinneret and the surface of the collector. This distance has a direct effect upon the fibre morphology as well as fibre diameter [169] since it determines the time of the flight of the electrospinning jet as well as the strength of the electric field [203]. When the tip-to-collector distance is too short, there is inadequate evaporation of the solvent caused by a shorter length of flight [203]. As a result the fibres stick to adjacent fibres and to the collector [172] and beading is also observed [169, 203, 217-219]. This decrease in the tip-to-collector distance can be considered as increasing the electric field strength since the field is acting over a smaller region [183, 220, 221]. Conversely, when the tip-to-collector distance is increased, the length of time of the flight of the jet is increased thereby allowing the solvent to evaporate sufficiently. The fibre is able to stretch to a greater extent and collect in fibres of smaller diameter [203]. The reasoning behind this observation is that the electrospinning jet is subjected to the electric field for a longer period of time due to the increased distance to the collector thus the fibre is stretched to a greater extent [222]. Therefore, there exists an optimum distance for fibre formation which allows for sufficient drying of the fibre. If this distance is significantly exceeded, beading will be observed in the collected fibres, or electrospinning could be unsuccessful [169].

4.5.5. Applied voltage

The optimum applied voltage or potential difference depends on the properties of the polymer solution itself [172]. It is of paramount importance to determine the correct voltage at which the Taylor cone and thus fibre formation occurs. If the voltage is below this critical point, the magnitude of the resulting electric field will be inadequate to induce electrospinning [169] since it will not be able to overcome the surface tension of the polymer solution [203].

The applied voltage used for electrospinning is generally determined by the capacity of the high voltage power supply, however, voltages exceeding 25 kV have not been reported and the

minimum voltage is typically 5 kV [182, 192]. It has been reported that the average diameter of the electrospun fibres increases slightly with an increasing applied DC voltage as the solution will be repelled away from the spinneret at a faster rate in the presence of a stronger electric field. Therefore the fibres will be drawn to a lesser extent and would result in larger average fibre diameters [192]. However, contrary to these findings, it has also been reported that increasing the magnitude of the applied voltage would result in narrower fibres since the increased electric field strength would subject the electrospinning jet to greater forces of repulsion thereby drawing the jet into narrower fibres. This is the more common observation [169, 187, 203, 223]. Thus, considering the net effect of the two aforementioned factors, the effect of the applied voltage on the morphology of the fibres is not significant [203] provided the applied voltage lies above that of the critical voltage at which electrospinning begins.

An additional consequence of a higher applied voltage is the formation of beads on the fibres [187, 206]. This bead formation is caused by jet instability [195] which is a result of the change in the shape of the Taylor cone itself. At lower voltages, the cone forms at the very end of the droplet of solution, however, at higher voltages the cone is formed at the tip of the spinneret. If this voltage is increased any further, the cone will form within the spinneret itself and result in beading of the fibres [206, 207]. Therefore, the optimum applied voltage is that which lies above the critical voltage and results in fibres of the desired diameter with little or no beading.

4.6. Ambient parameters

The processing parameters involved in the electrospinning process have already been discussed. Since electrospinning is typically conducted at room temperature under ambient conditions, the effects of temperature and humidity must also be considered.

Mit-uppatham *et al.* [209] found that an increase in the temperature at which the electrospinning is conducted led to fibres with decreased average diameters. This is a direct consequence of the inverse relationship between viscosity and temperature [169]. Temperature also has an effect on the evaporation rate of the solvent. It has been found that both low and high temperatures result in a decrease in the diameters of the fibres [224]. At low temperatures, the rate of evaporation is much slower therefore the electrospinning jet is exposed to the electric field for a longer period of time and can be drawn into a fibre of smaller diameter. At higher temperatures the effect of temperature on the solution viscosity dominates since the electric field would not be opposed by the viscous forces to the same extent. Therefore thinner fibres would be produced [224].

DeVrieze *et al.* [224] investigated the influence of ambient parameters on fibres where water is the solvent. They found that at high levels of humidity (60 %), individual fibres could not be formed and instead combined on the collector. This was caused by the presence of excess

absorbed water which resulted in inadequate drying of the solvent during electrospinning. For fibres with solvents other than, it was found that the diameters of the fibres decreased for increasing levels of humidity since this resulted in a slower rate of evaporation due to the presence of the absorbed water. Therefore, the fibre could be drawn to a greater extent prior to deposition on the collector [224].

Casper *et al.* [225] investigated the effects of humidity on the fibre morphology of fibres which do not absorb water. They found that higher levels of humidity (above 30 %) result in the formation of pores on the surface of the fibres. The size and prevalence of these pores increase with increasing humidity. The pores are formed due to the presence of condensed water droplets on the surface of the fibres which form when the electrospinning jet cools and the solvent evaporates, leaving behind a pore upon evaporation of the water [225]. The formation of these pores can prove to be beneficial if, for example, the intended application requires electrospun fibres possessing larger surface area or if the fibres are used in drug-related applications in which case the pores can be used to house nanoparticles [225].

4.7. Characterization of electrospun fibres

The geometry of electrospun fibres is typically analysed through Scanning Electron Microscopy (SEM) and Field Emission Gun Scanning Electron Microscopy (FEG-SEM) [172, 225] as this microscopy is capable of revealing the fibre morphology in the submicron range [169, 191, 192]. The fibre samples are usually coated in gold or carbon to prevent charging and damage to the sample [192, 203, 225]. SEM allows any beading or pore formation of the fibres to be examined and also allows the average diameter of the electrospun fibres to be determined [170, 225]. Furthermore, lower magnifications of the collected fibre samples provides an indication of the dispersion of the fibres thereby enabling the effect of the various processing and solution parameters to be investigated and tuned accordingly [171]. Figures 4-3 to 4-6 depict various SEM and FEG-SEM images of electrospun fibres. It can be seen from these images that SEM provides detailed micrographs of the fibre morphology and any defects can be clearly seen; this allows for a relatively simple investigation of the effects of the various electrospinning parameters on the fibre morphology to be conducted.

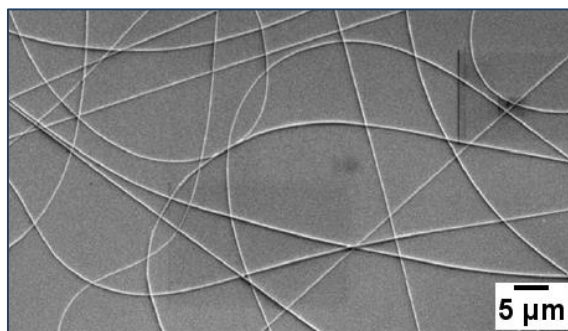


Figure 4-3 Typical SEM image of electrospun graphene/PVA composite fibres [193].

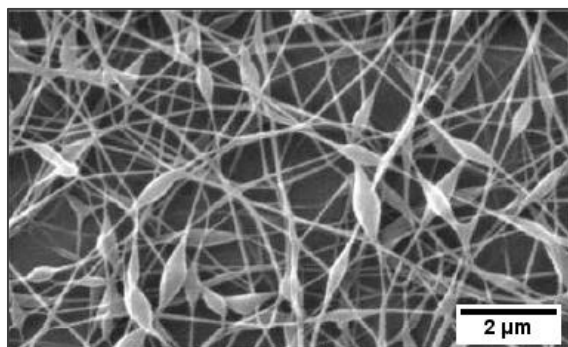


Figure 4-4 SEM image of electrospun PVA with visible beading present [192].

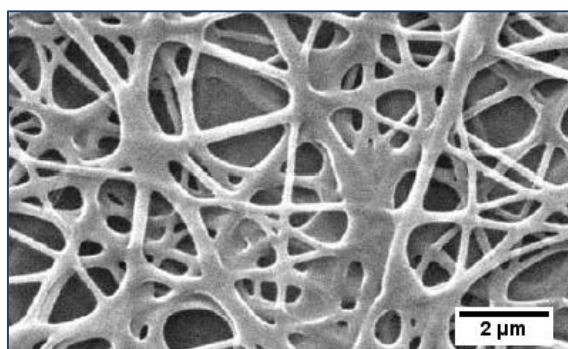


Figure 4-5 SEM image of electrospun PVA depicting a web-like deposit [192].

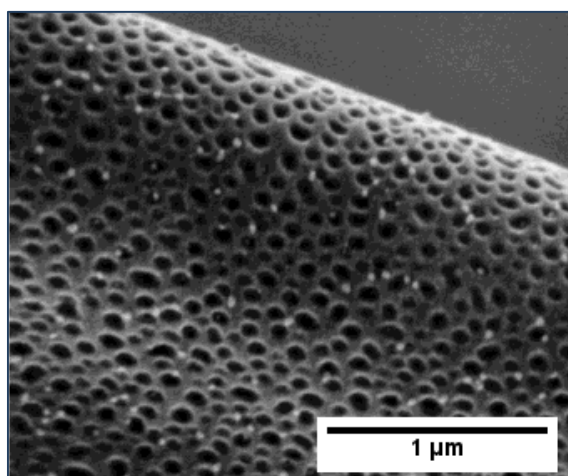


Figure 4-6 FEG-SEM image of electrospun polystyrene/THF fibres with visible pores present [225].

There are other means with which to characterise the properties of electrospun fibres, such as chemical characterisation through the use of Fourier-Transform Infrared Spectroscopy (FTIR) to determine the composition and inter-molecular structure of the fibres. Mechanical properties can be characterised through tensile loading of the electrospun fibres [169, 172]. However, such characterisation techniques are not necessary for the purposes of this research. Therefore, they shall not be discussed here.

4.8. Applications of electrospun graphene/PVA composite fibres

Fibres produced via electrospinning are highly versatile as they can be fabricated from a number of precursor materials and can be tailored to the need of the user. Electrospun fibres can be used in biomedical, filtration and electrical applications, to name a few [172]. However, the focus of this research is on graphene/PVA composite fibres. Therefore, only select applications pertaining to these fibres are discussed in this section.

As previously stated, conductive nanofibres were successfully produced through the electrospinning of carbon nanotubes and polymer composites [168]. The resulting fibres could be used to produce electrodes for electroactive polymer actuators due to their conductive properties as well as their high surface-area-to-volume ratio which would improve the rate of the electrochemical reactions [168]. These electrospun fibres can be used in many forms in energy related-applications such as in batteries, fuel cells and solar cells [226].

PVA has recently been electrospun together with graphene and the addition of graphene to the polymer solution greatly improved the mechanical strength and thermal properties of the resulting electrospun fibres even when small amounts of graphene was added [190, 193, 227]. Das *et al.* [193] electrospun pristine graphene in an aqueous solution of PVA. The resulting fibres demonstrated greater thermal stability and crystallinity. Liang *et al.* [227] used graphene oxide, rather than graphene. The study found that a low loading of GO (0.7 wt. %) resulted in significant improvement of the fibres' tensile strength and Young's modulus when compared with pure PVA fibres. The study by Liang *et al.* [227] showed that the use of water as the solvent for the polymer solution enabled the molecular-level dispersion of the GO in solution which allowed for reinforced composite nanofibres to be formed. Wang *et al.* [190] reported similar findings with graphene and GO loaded PVA composite nanofibres. It was also found that the fibres displayed a degree of hydrophobia. This is highly advantageous since pure PVA fibres are hydrophilic [190]. Therefore, the addition of graphene to these fibres removes the limitations on the applications of PVA nanofibres. This study found that graphene does not easily disperse when directly added to the PVA solution. Therefore, GO was added to the solution first and later chemically reduced to form graphene which was uniformly dispersed [190].

The resulting graphene/PVA electrospun fibres can be used in numerous applications, such as electrodes, conductive wires, fuel cells as well as for biomedical uses [193]. Composite GO loaded fibres can also be used as a load-bearing filler to form nanocomposite materials [227].

4.9. Summary

Electrospinning is a relatively simple process to execute. Nanofibres consisting of a wide variety of materials may be fabricated using this method. The two, primarily discussed polymers here are PVA and polystyrene. It was found that the advantage of PVA over polystyrene is that PVA is readily soluble in water while polystyrene is only soluble in solvents such as DMF and amyl acetate which are potentially hazardous, therefore the PVA electrospinning route is more environmentally friendly. In addition, when water is used as the solvent for the polymer solution, the graphene or GO is uniformly dispersed at the molecular level which allows for the production of fibres with superior strength characteristics [227].

While electrospinning may be a simple process to perform, several factors influence the morphology of the fibres produced. These factors are subdivided into three main groups: solution, processing and ambient parameters. These parameters do not act in isolation therefore the process of optimising the electrospinning process for a desired fibre morphology can be an arduous and time consuming process.

Chapter 5 Synthesis of graphene

The scope of this research entailed the investigation of five different experimental methods used to synthesise graphene oxide (GO) in order to determine which method produced GO with the highest quality as well as the method which would be most suitable for producing GO in the Materials Science Laboratory at the School of Engineering in UKZN. The quality of the GO was determined by the extent of topological defects, the surface area, and the degree of oxidation. The samples were analysed using electron microscopy, EDS and XRD to determine the quality thereof. The GO samples resulting from each of these methods were compared based on the degree of oxidation of each sample. The graphene produced was characterised by comparing the degree of reduction (or deoxygenation) of the samples. As previously mentioned, the chemical approach was adopted as opposed to the “Scotch tape” method which would not produce large quantities required by the various projects in the laboratory. The first investigated method was the Hummers’ method [12, 57]. This is the most common method used to prepare graphene oxide and is one of the first methods which resulted in the production of so-called “graphitic oxide” [57]. At the time of its inception, the Hummers’ method was considered to be relatively safe in comparison to the Brodie synthesis of GO [228] and the Staudenmaier method [229] which were both considered severely time consuming and hazardous [57]. The Brodie method involves treating graphite powder with potassium chlorate in fuming nitric acid [228]. The Staudenmaier method is similar to the Brodie method. The graphite powder is treated with potassium chlorate in fuming nitric acid and concentrate sulfuric acid [229]. The product resulting from the Hummers’ method is more oxidized than that of the Brodie method [228]. The products of the Hummers’ and Staudenmaier methods are comparable, however, the oxidation is achieved within approximately 2 hours for the Hummers’ method versus a week for the Staudenmaier method [229].

However, the Hummers’ method also involves the production of toxic gases, such as dinitrogen tetroxide and nitrogen dioxide, and the yield of GO resulting from this method is low in comparison to alternative methods, such as the Tour method [12]. Therefore, different experimental methods were investigated in order to produce larger amounts of highly oxidized GO by safer means. These methods make use of many of the Hummers’ reagents with a few

modifications. The purpose of conducting these additional methods was to compare the resulting quality of GO in order to determine the most efficient method as well as the method most suited for the production of GO in the Materials Science Laboratory at the School of Engineering in UZKN.

5.1. Experimental methods

Different synthesis approaches were used, however the purification procedure used for each of these methods was identical. This procedure is expanded upon in Section 5.2. Each of the five experimental methods made use of the same quantity of coarse grade natural flake graphite (3.0 g) of mesh size $\sim 150\ \mu\text{m}$ from RMC Minerals as a starting material so as to standardise the experiments and enable the comparison of the results. Furthermore, the use of natural flake graphite as opposed to graphite powder ensured that high quality GO was produced [12] as the inherent defects present in its structure are believed to act as seed points for the oxidation reaction [70]. The small flakes of graphite provide a large surface area for the oxidation reactions [111]. The oxidising agents used in the experiments included potassium permanganate (KMnO_4) and sodium nitrate (NaNO_3) [70]. While KMnO_4 is an oxidising agent, the primary oxidant is actually diamanganese heptoxide (Mn_2O_7) which forms as a result of the reaction between KMnO_4 and sulphuric acid (H_2SO_4) [70]. Mn_2O_7 is highly reactive and will ignite if heated above $55\ ^\circ\text{C}$ [70] therefore the temperature of the reaction must be kept below this point. The oxidation reaction in each of the experiments was ended by the addition of hydrogen peroxide (H_2O_2) to the mixture. This also serves to remove residual salts from the GO mixture.

5.1.1. Hummers' method

The Hummers' method is the classic and most well-known method of synthesising GO. The method as described in [12] was followed. The amounts of the various reagents used in the experiment are shown in Table 5-1.

Table 5-1 Reagents used in the Hummers' method experiment.

Material	Quantity
Natural flake graphite	3.02 g
Sodium nitrate (NaNO_3)	1.53 g
Potassium permanganate (KMnO_4)	9.00 g
Concentrated sulphuric acid (H_2SO_4 , 98 %)	69 ml
Distilled water	138 ml + 420 ml
Hydrogen peroxide (H_2O_2 , 30 %)	3.00 ml

Concentrated H_2SO_4 was added gradually to a mixture of graphite flakes, NaNO_3 and KMnO_4 . This mixture was subjected to constant stirring while placed in an ice water bath at a temperature of $4\ ^\circ\text{C}$. The acid was added to the mixture containing KMnO_4 instead of vice versa

as this was the safer method. If KMnO_4 is added rapidly to the acid, this could result in an explosive reaction. Furthermore, by adding the acid slowly in small amounts to the mixture, this ensured that the temperature of the reaction did not exceed $20\text{ }^\circ\text{C}$. The temperature of the bath immediately after the addition of the acid was $16\text{ }^\circ\text{C}$. The temperature of the mixture was approximately $20\text{ }^\circ\text{C}$. It was observed that the mixture gradually changed to a deep green colour due to the presence of the KMnO_4 in the acid [230]. Once all the acid was added, the resulting mixture was heated to $35\text{ }^\circ\text{C}$ and stirred for a further 30 minutes. Distilled water was then added gradually to the reaction which produced an exothermic reaction. The water was added gradually in order to ensure that the reaction continued to completion and reached a temperature of $98\text{ }^\circ\text{C}$. At this point, the reaction was maintained at $98\text{ }^\circ\text{C}$ and stirred for another 15 minutes after which the beaker containing the mixture was placed in a water bath to cool for 10 minutes. The reaction was stopped by adding distilled water together with H_2O_2 . This too produced a slightly exothermic reaction. The mixture was purified as described in Section 5.2 after cooling to room temperature.

5.1.2. Modified Hummers' method with extended oxidation time

The second method is a modified version of the Hummer's method, based on "Hummers' method +" as described in [12]. The experimental procedure for "Hummers' method +" was further modified to investigate the effects of extending the oxidation time and the addition of extra KMnO_4 individually. The first stage of the experiment was identical to that of the Hummers' method, however, the mixture was left to stir overnight once all the acid was added. This served to extend the oxidation time available for the reaction. After the oxidation period, it was observed that the mixture was uniformly brown in colour, indicating a high level of oxidation [230]. The solution was also more viscous than in the first method. This could have been caused by partial evaporation of the liquid component of the solution. This could be avoided in future experiments by covering the reaction vessel. Another more likely cause would be due to the increased surface area of the material present in solution which might have been caused by the chemical exfoliation of graphite to form GO. This increase in the surface area of the material present would have increased the viscosity of the solution.

The method thereafter was identical to that of the Hummers' method from the point at which distilled water was added. This process is detailed above. Table 5-2 indicates the amounts of each reagent used in this experiment.

Table 5-2 Reagents used in the Modified Hummers' method with extended oxidation time.

Material	Quantity
Natural flake graphite	3.01 g
Sodium nitrate (NaNO_3)	1.51 g
Potassium permanganate (KMnO_4)	8.99 g
Concentrated sulphuric acid (H_2SO_4 , 98 %)	69 ml
Distilled water	138 ml + 420 ml
Hydrogen peroxide (H_2O_2 , 30 %)	3.00 ml

5.1.3. Modified Hummers' method with additional potassium permanganate

The third method is also a modified version of the “Hummers' method +” presented in [12]. However, the effect of adding extra KMnO_4 was investigated in this experiment. An additional 9.02 g of KMnO_4 was added during the oxidation stage. Table 5-3 indicates the amounts of each reagent used in this experiment.

Table 5-3 Reagents used in the Modified Hummers' method with additional potassium permanganate.

Material	Quantity
Natural flake graphite	3.02 g
Sodium nitrate (NaNO_3)	1.51 g
Potassium permanganate (KMnO_4)	8.99 g + 9.02 g
Concentrated sulphuric acid (H_2SO_4 , 98 %)	69 ml
Distilled water	~400 ml
Hydrogen peroxide (H_2O_2 , 30 %)	3.00 ml

The first stage of the experiment was largely similar to that of the Hummers' method in terms of the reagents used and the executed method. Concentrated H_2SO_4 was added gradually in very small amounts to a mixture of the graphite flakes, NaNO_3 and KMnO_4 . This mixture was subjected to constant stirring while placed in an ice water bath at a temperature of 4 °C. It was observed that the mixture gradually changed to a deep green colour. Once all the acid was added, the resulting mixture was heated to 35 °C and stirred for 2 hours. The mixture was cooled to room temperature and left stirring overnight. This acted as a safety precaution to ensure that all the acid was reacted before adding a further 9.0 g of KMnO_4 . After this oxidation period, it was observed that the mixture was light brown in colour indicating a high level of oxidation [230].

Additional KMnO_4 was added all at once to the mixture while stirring. The mixture was heated to 35 °C and left to stir for another 16 hours. After this period, the mixture was much browner in colour than that of the mixtures from the previous two experiments. This indicated that the degree of oxidation of this mixture was higher than that of the previous two methods [230]. After the addition of the KMnO_4 and the 16-hour period of stirring, the mixture was left to cool to room temperature and then poured onto approximately 400 ml of ice together with 3.0 ml

of H_2O_2 . This stopped the reaction. The mixture was purified as described in Section 5.2 after cooling to room temperature.

5.1.4. Tour method

The Tour method is an adaptation of the traditional Hummers method which makes use of a mixture of sulphuric acid (H_2SO_4) and phosphoric acid (H_3PO_4) in a 9:1 ratio [12]. This avoids the production of the toxic gases produced during the various Hummers' methods. The method as detailed in [12] was followed and the amounts of the various reagents used in the experiment are presented in Table 5-4.

Table 5-4 Reagents used in the Tour method experiment.

Material	Quantity
Natural flake graphite	3.02 g
Potassium permanganate (KMnO_4)	18.01 g
Concentrated sulphuric acid (H_2SO_4 , 98 %)	360 ml
Concentrated phosphoric acid (H_3PO_4 , 85 %)	40 ml
Distilled water	~ 400 ml
Hydrogen peroxide (H_2O_2 , 30 %)	3.00 ml

The two acids were mixed together and thereafter added gradually to a mixture of graphite flakes and KMnO_4 . This produced an exothermic reaction. The mixture was cooled in an ice water bath at 4 °C. This produced an exothermic reaction. The mixture was then heated to 50 °C and left stirring for approximately 19 hours. After this period, the mixture was black in colour and was giving off purple/brown fumes. These fumes were produced from the oxidation reaction involving the potassium permanganate. The mixture was left to cool to room temperature and thereafter poured onto approximately 400 ml of ice together with 3.0 ml of H_2O_2 . The resulting product was cleaned as per the method discussed in Section 5.2.

The advantages of this method included: no toxic gas production during the experiment, a simpler experimental procedure compared to the previous three methods, and a higher yield of GO compared to the Hummers' method and modifications thereof. These advantages make this method a potentially viable means with which to produce GO on a large-scale.

5.1.5. Huang method

The simple room-temperature preparation of graphene oxide (Huang method) is also a modified version of the traditional Hummers' method involving a simpler approach towards attaining GO than the previously discussed methods [102]. This method has been found by Huang *et al.* [102] to produce large GO flakes with a higher degree of efficiency. The large-area flakes of GO were achieved by using relatively large graphite flakes as the precursor material. It was found that the size of the GO flakes increased as the ratio of KMnO_4 to the acid was increased

[102]. The primary advantage of this method over the other four methods was that the time spent doing physical experimental work was far less than the other reported methods since the mixture was allowed to react unattended without the need for temperature control for a period of three days [102].

Huang *et al.* [102] reported that this experiment is quite safe, and that the likelihood of an explosive reaction is minimal. However, this was found not to be the case as the first attempt resulted in an explosive reaction and energetic fuming of the solution. This was most likely caused by the reaction between the KMnO_4 and the acids [70]. The reagents used in the second attempt of this experiment are presented in Table 5-5.

Table 5-5 Reagents used in the Huang method experiment.

Material	Quantity
Natural flake graphite	3.00 g
Potassium permanganate (KMnO_4)	18.02 g
Concentrated sulphuric acid (H_2SO_4 , 98 %)	320 ml
Concentrated phosphoric acid (H_3PO_4 , 85 %)	80 ml
Distilled water	~350 ml
Hydrogen peroxide (H_2O_2 , 30 %)	3.00 ml + 3.00 ml

For the second attempt, the graphite and KMnO_4 were crushed using a mortar and pestle prior to their addition to the beaker to avoid an explosive reaction. While it was understood that this would reduce the likelihood of large GO flakes, it was deemed necessary as a safety precaution. The reaction beaker was also placed in an ice water bath to lower the temperature of the reaction. While the method as per [102] did not require any temperature control, this was added as a precautionary measure. The two acids were then mixed together and added very slowly in miniscule amounts directly to the area of the rotating stirrer bar, however, after approximately 20 ml of acid had been dispensed, aggressive fuming of the mixture resulted once again. The possible cause of this was the presence of a larger quantity of H_3PO_4 as compared to the Tour method. Another possible cause was that the ice water bath was not sufficiently cold, and a slurry of ice and water should have been used instead. The mixture was not discarded since the observed fuming was not as aggressive as the previous attempt and the mixture still appeared a favourable brown colour rather than brownish-black as observed following the fuming of the previous attempt.

The reaction beaker was immediately placed in a fresh ice water bath once the fuming had lessened in order to lower the temperature of the exothermic reaction so that the experiment could proceed. Thereafter, the remaining acid was added gradually to the mixture under constant stirring once again. However, the purple-brown smoke as observed during the previous experiments was not observed during this stage. Following the incorporation of the remaining acid, the mixture was brown in colour rather than purplish-green as expected [102]. The most likely cause for this

colour change was the aggressive reaction which took place during the early stages of the experiment. The mixture was then left to stir for three days as per the method in [102].

After stirring for three days, the mixture was very dark brown in colour. The H_2O_2 was then added together with ~350 ml of distilled water to stop the oxidation reaction. This did not result in the expected colour change to lighter brown. At this point, the pH of the solution was measured as 0.35 pH. Hence, another 3.0 ml of H_2O_2 was added to reduce the acidity of the solution and to achieve the expected colour change. The mixture remained very dark brown upon this second addition of H_2O_2 , however, when ~5 ml of the solution was diluted in ~100 ml of distilled water, a yellow-brown colour was observed thereby indicating that oxidation had occurred [230]. The resulting mixture was then purified as detailed in Section 5.2.

The synthesis of GO as described in [102] entails the washing of the resulting GO with only hydrochloric acid (HCl) and deionized water, however for consistency, the washing method as detailed by Marcano *et al.* [12] and in Section 5.2 was used for all five experiments.

5.2. Method of washing of graphene oxide

The resulting product from each experiment was firstly filtered through a qualitative filter paper with an 11 μm pore size (Whatman filter paper). The filtrate was discarded. The solid on the filter paper was first washed with 200 ml of distilled water and centrifuged at 4000 rpm for 20 minutes and the supernatant was discarded. Three more washes followed in succession: once with 200 ml of 32 % hydrochloric acid (HCl) and twice with 200 ml of ethanol. After each wash, the mixture was centrifuged at 4000 rpm for 15 minutes and the liquid was discarded. The HCl wash was used to remove the residual metal salts from the KMnO_4 and NaNO_3 . The ethanol washes assisted in drying the GO.

In Section 3.5 the degradation of graphene as well as GO was explored. It was found that graphene degrades in the presence of H_2O_2 and that GO also degrades by enzymatic action in the presence of H_2O_2 [114, 119]. The washing of GO removes the H_2O_2 used to end the oxidation reaction therefore this compound is no longer present in the product itself. Furthermore, the GO produced from each experiment was stored in a desiccator, therefore the risk of degradation by H_2O_2 was greatly lessened.

5.3. Observations

The following section entails descriptions of noteworthy observations made throughout the various experiments. Many of these observations include a colour change of the solution. As previously discussed, a yellow-brown solution indicated a high level of oxidation and hence a product of a higher quality, while darker green-black coloured solutions indicated GO which has

a low level of oxidation or it may indicate the presence of unreacted graphite. This was taken to indicate a lower quality product [230].

Hummers' method

Prior to the washing of the synthesised GO using the Hummers' method, it was clearly seen that a significant amount of unreacted graphite was still present in the form of a dark solid material. This can be seen in Figure 5-1. After the oxidation reaction was stopped by the addition of distilled water and H_2O_2 , the solution was left to stand for ~3 hours. At the end of this period, a light yellowish-brown layer was observed as seen in Figure 5-1, however, a very dark brown-black layer was also seen at the bottom of this beaker. This layer was larger than the lighter brown top layer thereby indicating that there was a substantial amount of unreacted graphite present. Upon filtration of the solution, this was seen more clearly. The solid from top layer of the solution was yellowish-brown. The colour slowly progressed to a green-black colour in the middle. Eventually the bottom layer of the solution yielded a very dark solid. This result shows that the more oxidised material is less dense since it settles in the upper part of the solution, as expected due to the wider interlayer spacing [58, 59]. These images can be seen in Figure 5-2. Furthermore, the filtrate was light pink in colour which indicated that the excess KMnO_4 remaining in the solution was filtered out of the solid material.



Figure 5-1 GO produced via the Hummers' method prior to washing.

The Figure 5-2 shows the GO solids attained from the synthesis of GO via the Hummers' method. The progression of the colour change can be clearly seen. Figure 5-2 (a) is of the light yellow-brown top layer of GO solution. Figure 5-2 (b) is of the layer immediately below that and appeared green due to the presence of some of the highly oxidised yellow-brown GO as well as less oxidised product thereby giving it this appearance. Figure 5-3 (c) is similar to the previous image however it can be seen that there was a larger amount of the less oxidised product due to its darker colour [230]. Lastly, Figure 5-3 (d) is very dark and almost black thereby indicating that this part of the solid consisted of mostly unreacted graphite or less oxidised GO [230],

however, it did exhibit yellow-brown colouring around its edges which indicated the presence of some oxidised material.

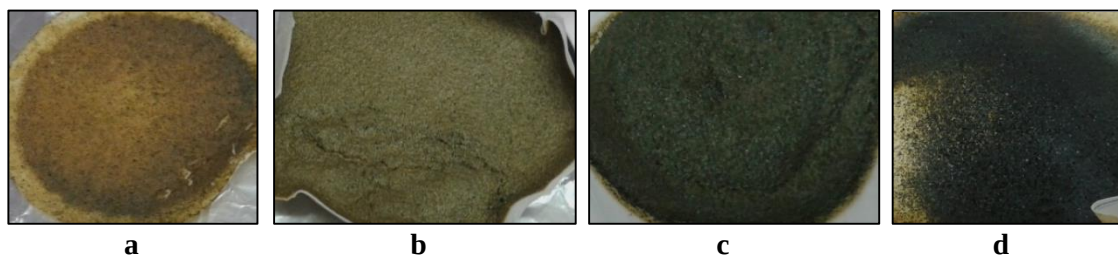


Figure 5-2 Solid GO collected following the filtration of GO produced via the Hummers' method. The various different colours of the solids indicate the area of the solution from which they were filtered: lightest yellow-brown solid (a) - upper part; light green-brown solid (b) - upper middle part; dark yellow-brown solid (c) – lower middle part; and dark brown-black solid (d) – lower part.

During the washing process, it was observed that the clear HCl turned yellow following centrifugation which indicated the presence of the various salts in the supernatant that was discarded. The same observation was made during the ethanol washes, however, the supernatant was much clearer following the second ethanol wash. The ethanol served to substantially dry the solid GO produced.

Modified Hummers' method with extended oxidation time

Following the extended oxidation time of 24 hours, as specified for this method, the resulting GO solution was uniformly brown which can be seen in Figure 5-3. The yellow-brown solid was not observed for this experiment, however, it should be noted that the yellow-brown solid was only observed once the solution had been left standing for several hours while the solution as seen in Figure 5-3 has been subjected to constant stirring. Therefore, the various constituents of the solution have been evenly distributed throughout the solution. Although, this brown colour did still indicate the presence of highly oxidised material.

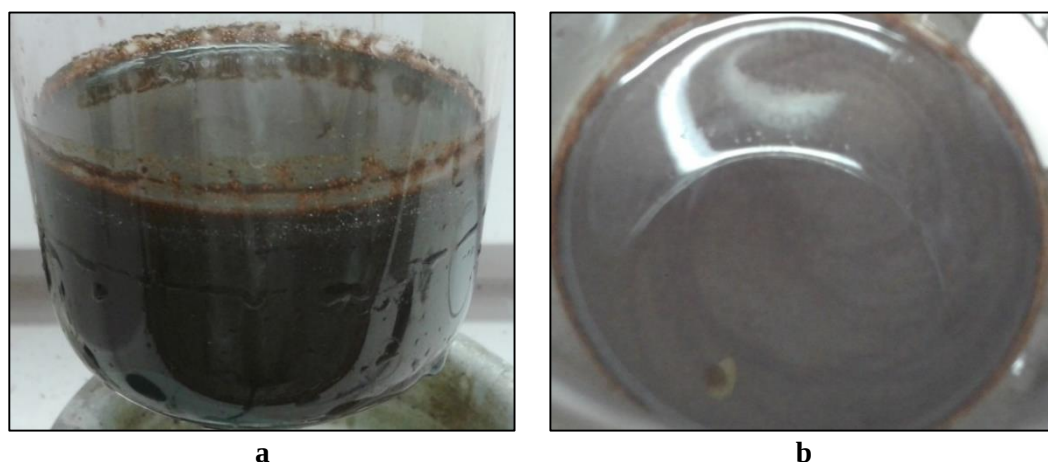


Figure 5-3 GO produced via the modified Hummers' method with extended oxidation time prior to washing. Side view (a) and top view (b).

Following the washing process, the GO could easily be distinguished from the unreacted graphite since the GO was brown in colour while the graphite was silvery grey. This can be seen in Figure 5-4 (b). This figure shows how the brown colour of the solution was diminished slightly following the washing process as residual salts were washed out and the solid was dried. The result was that the GO could be more easily discerned from the graphite (if present in the solid).

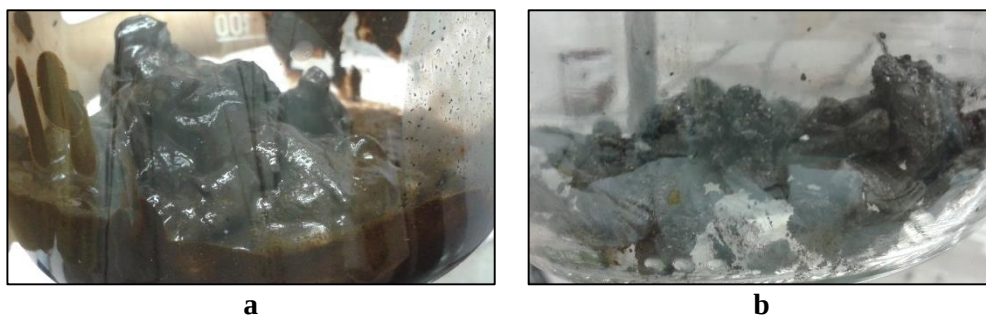


Figure 5-4 GO obtained from the modified Hummers' method with extended oxidation time (a) after water wash and (b) after second ethanol wash.

Modified Hummers' method with additional potassium permanganate

After the completion of the oxidation reaction, the solution was brown after stirring, as depicted in Figure 5-5. This solution was lighter brown than the previous experiment thus indicating a greater degree of oxidation [230].

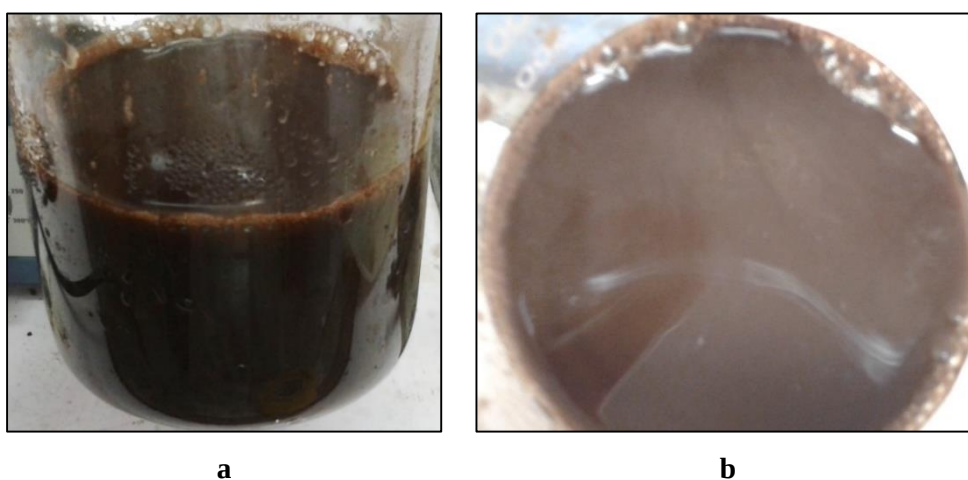


Figure 5-5 GO produced via the modified Hummers' method with additional KMnO_4 prior to washing. Side view (a) and top view (b).

During filtration of the GO solution produced using this method, it was observed that the filtrate was darker pink to almost red in colour. This was expected as the amount of KMnO_4 used during this experiment was twice as much as that used for the previous two experiments and it was the presence of the KMnO_4 which gave the filtrate this pink hue.

During the washing process, the solid became darker after each successive wash. It was noted that the HCl wash in particular seems to make it easier to distinguish the less oxidised material from the highly oxidised material within the solid. This can be seen in Figure 5-6 (a).

There are distinguishable areas of yellow-brown material and darker brown-black material, indicating highly oxidised and less oxidised material, respectively [230]. It is difficult to identify these distinct areas of different levels of oxidation once the final wash with ethanol has been carried out, as seen in Figure 5-6 (b). This is due to the solid material collecting in clumps following the drying effect of the ethanol wash thus individual clusters are difficult to identify.

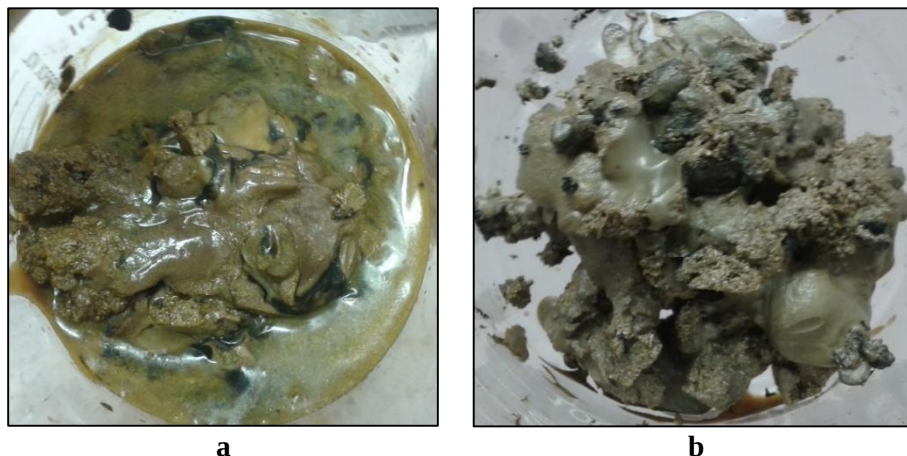


Figure 5-6 GO produced from the modified Hummers' method as it appeared after the HCl wash (a) and after the final wash (b).

Tour method

Once the oxidation reaction had continued to completion, the resulting GO produced was significantly lighter brown than that produced via the previous three experiments. This indicates a high degree of oxidation [230]. The light brown colour (when compared to that of the other experiments) of the solution can be seen in Figure 5-7. The image provides an indication of the true colour of the GO produced using this method as the solution had been sufficiently stirred to distribute the solid material evenly.

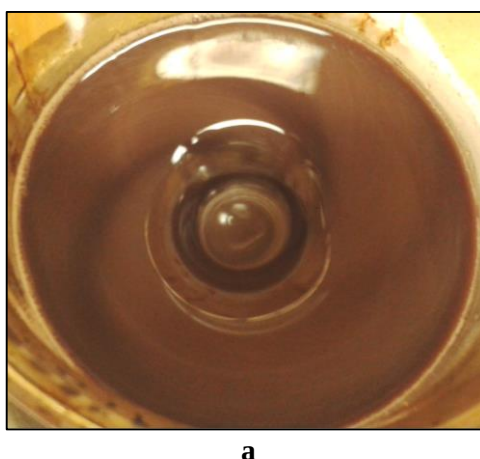


Figure 5-7 GO produced via the Tour method prior to washing, while stirring.

When it was attempted to filter the GO produced, the mixture proved to be highly acidic since it dissolved the filter paper. Therefore, to neutralize this acidity, a medium strength base

(sodium carbonate) was used. A solution was prepared using 10.01 g of sodium carbonate dissolved in ~100 ml of distilled water. This basic solution was added to the GO solution and it was attempted to filter this solution once again. However, the solution was still too acidic as holes were created in the filter paper through acidic action. Therefore, another basic solution was prepared by dissolving 5.02 g of sodium carbonate in ~50 ml of distilled water and thereafter adding this solution to the GO. This further addition proved successful in neutralizing the pH of the solution which was then filtered successfully. Note that the sodium carbonate residue was also removed via the washing of the GO solution. Immediately after the filtering of the GO mixture, a bright yellow-brown solid was obtained. This can be seen in Figure 5-8. It appeared that the dark pink colour of the KMnO_4 in solution obscured the true colour of the GO. This result is consistent with the findings of Marcano *et al.* [12] and indicated the high level of oxidation of the GO obtained using this method.

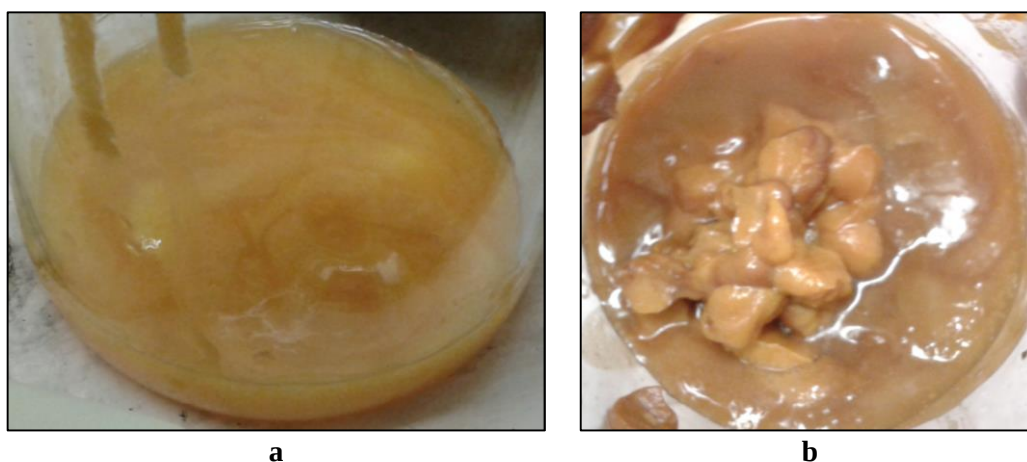


Figure 5-8 Yellow-brown solid obtained immediately after filtering.

It was observed that the colour of the solid gradually changed to become more brown during the washing process. During the first wash with distilled water, it was observed that the solid obtained was very brown. Unlike in the previous experiments, this colour was homogenous throughout the solid. This indicated that the majority, if not all of the GO produced during this experiment was oxidised adequately since no obvious evidence of darker areas of graphitic particles was found [230]. The final GO obtained maintained this homogenous brown colour, as depicted in Figure 5-9, however, it was apparent that the ethanol had less of a drying effect on this GO than on the previous products. This could be a consequence of the structure of the highly oxidised GO as it is easily dispersed in water as well as suitable, organic solvents [64, 65] and it seemed that ethanol is one such solvent.



Figure 5-9 GO obtained via the Tour method after the final ethanol wash.

Huang method

Following the 3-day oxidation period required for the Huang experiment, the mixture was very dark brown in colour. However, when H_2O_2 and distilled water was added to the mixture to stop the oxidation reaction, no colour change was observed. At this point, another 3.0 ml of H_2O_2 was added to reduce the acidity of the solution and to achieve the expected colour change to a lighter brown. The mixture became slightly lighter brown upon the addition of the extra H_2O_2 . This very subtle colour change can be observed in Figure 5-10. When the solution was diluted by dissolving ~ 5 ml of the GO solution in ~ 100 ml of distilled water, a noticeable yellow-brown colour was observed, as seen in Figure 5-11 below. This indicated that oxidation had occurred [230]. Although, fine, black particles were also observed in the diluted solution which indicated the presence of less oxidised material [230].



Figure 5-10 GO solution upon the addition of 3.0 ml of H_2O_2 (a) and 6.0 ml (in total) of H_2O_2 (b).

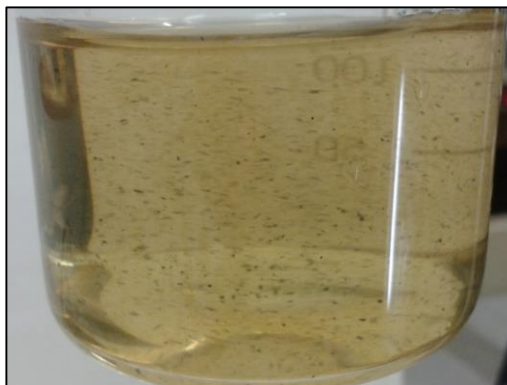


Figure 5-11 Yellow-brown appearance of GO solution.

During the washing process, it was observed that the synthesised GO was more black than brown in colour. Prior to centrifugation of the GO suspended in ethanol during the last washing step, visible shiny, floating particles were observed in the mixture. This suggested that unreacted graphite was present in the mixture due to the appearance of the floating particles. This under-oxidation of the material could have been caused by the explosive reaction. The resulting GO solid produced using this method was far darker in colour than those from the other four methods, as can be seen in Figure 5-12 below. The dark, mostly black appearance of the GO produced using this method indicated that the oxidation level of this product was fairly low [230] in comparison to the other four methods.



Figure 5-12 GO obtained via the Huang method after the last ethanol wash.

5.4. Methods of reducing graphene oxide

The experimental reduction procedures are detailed in this section and some images have been provided which were taken during the various processes. However, the SEM and TEM as well as XRD data obtained from the reduction of the synthesised GO can be found in Chapter 7 along with an analysis of the products resulting from the individual methods. Two broad methods were explored to reduce the synthesised GO: via heat and via chemical reduction.

5.4.1. Reduction by sodium borohydride

The first approach towards reducing GO was the chemical approach. This approach is highly beneficial as it enables the graphene to be deposited onto any suitable substrate from solution [45]. As mentioned in Chapter 3, GO has successfully been reduced via hydrazine hydrate [63, 64] as well as anhydrous hydrazine [36] and sodium borohydride (NaBH_4) [74]. While the products resulting from the reduction of GO via hydrazine have extensively been explored and characterised [45, 63, 64], Yang *et al.* [74] reduced GO through the use of a different reducing agent, sodium borohydride. It has been found that NaBH_4 is the more effective reducing agent for GO since the resulting graphene produced using this method has a sheet resistance of $59 \text{ k}\Omega \cdot \text{sq}^{-1}$ whereas that produced using hydrazine has a sheet resistance of $780 \text{ k}\Omega \cdot \text{sq}^{-1}$ † [70]. Another advantage of this reducing agent over the commonly used hydrazine is that NaBH_4 is a nontoxic, noncorrosive and cheaper alternative [74] while hydrazine is toxic and potentially explosive [232, 233]. Another advantage of using NaBH_4 over hydrazine is that the experimental procedure is simpler in terms of its execution since the reduction reaction is conducted under ambient conditions [74] whereas the GO solution containing hydrazine must be heated to 100°C for the reduction reaction to occur [63]. Yang *et al.* [74] reported that the graphene produced via NaBH_4 exhibited low electrical resistance and a wrinkled appearance thus resulting in a smaller average flake size. The small flake size is a disadvantage of reduction via NaBH_4 as graphene with a large surface area is desirable for applications such as supercapacitors.

The method for reducing the GO via NaBH_4 was as follows: a 1 mg/ml solution of GO and distilled water was prepared and ultrasonicated for 30 minutes. Note that GO does not refer to any of the previously discussed methods in particular as this method of reduction was carried out on each of the five GO samples. This beaker was then placed in a fume cupboard and 4.56 g of NaBH_4 was added to the GO solution and left to stir at room temperature for 30 minutes. It was observed that the solution immediately became much darker in colour and bubbled aggressively upon the addition of the NaBH_4 . This colour change is depicted in Figure 5-13 below which shows the solution of distilled water and GO from the Tour method and the resulting black solution following the reduction reaction. After this period of time, the solution was ultrasonicated for 30 minutes. When the solution was left standing overnight to ensure the completion of the reaction, it was noted that a black precipitate had formed. This is an indication that the reduction of GO was successful since the removal of its surface functionality results in the formation of the hydrophobic, reduced GO [74]. Another $\sim 100 \text{ ml}$ of distilled water was added to the solution to wash any residual NaBH_4 out from the solution. This solution was then filtered using a vacuum

† Note that these units have been expressed as $\text{k}\Omega \cdot \text{sq}^{-1}$ rather than in $\text{k}\Omega$ so as not to represent an ambiguous quantity. The units of $\text{k}\Omega$ are often associated with the bulk resistance of a material while the units of $\text{k}\Omega \cdot \text{sq}^{-1}$ indicate the sheet resistance of a thin film [45] [231].

filter. Nylon membrane filters with a pore size of 0.45 μm and diameter of 47 mm were used. These filters were used since the particle size of the graphene is in the order of micrometres [234]. Also, the nylon membrane filters allow the solid to be more easily removed when compared to filter paper, as shown in Figure 5-13 (c). After the filtering of the solution, the rotary pump of the vacuum filter was left running for ~ 3 hours to facilitate drying of the graphene.

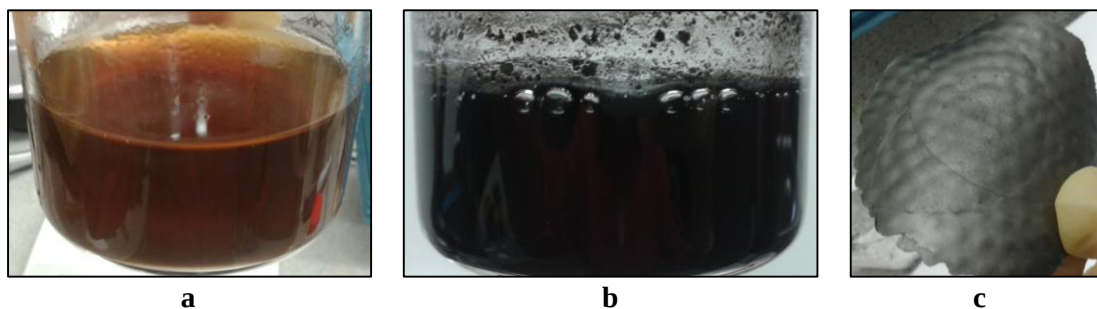


Figure 5-13 Colour change from the yellow-brown-colour of the GO solution (a) to the black colour following the reduction reaction via NaBH_4 (b) and the resulting filtered graphene (c).

5.4.2. Reduction via ascorbic acid

The need for the reduction via an alternative route was inspired by difficulties experienced during electrospinning. The primary concern of using NaBH_4 as the reducing agent was that it reacted unfavourably with the distilled water present in the electrospinning solution of aqueous PVA. Rapid bubbling was observed as a result of the reaction between the reducing agent and the distilled water [74] which caused the PVA solution to congeal thus rendering it unsuitable for electrospinning. This was a consequence of the inability to entirely remove the NaBH_4 from the solution. Hence a reducing agent which did not have an adverse reaction when exposed to water was investigated which led to the method of reducing GO via ascorbic acid. This is discussed further in Chapter 6 while the method shall be detailed here since it pertains to the reduction of graphene which is the focus of this section.

Ascorbic acid, otherwise more commonly referred to as vitamin C, is a naturally occurring antioxidant which is vital for the growth and repair of various tissues in living organisms and as such, it is nontoxic and completely water soluble [232, 233]. Due to these properties of ascorbic acid, it is the more environmentally friendly method of reducing GO when compared to both hydrazine and NaBH_4 . The solvent used for this method is distilled water and the reduction occurs under aggressive stirring or ultrasonication over a period of several hours after which time, Zhang *et al.* [233] showed that majority of the oxygen-containing functional groups had been removed. The effectiveness of ascorbic acid as a reducing agent for GO has been found to be comparable to that of hydrazine [232].

The method for reducing the GO via ascorbic acid was as follows: a 1 mg/ml solution of GO and distilled water was prepared and ultrasonicated for 30 minutes. Ascorbic acid (1.02 g) was weighed and added to the GO solution. There was no colour change observed immediately

after immediate addition of the ascorbic acid although the powder was completely dissolved upon stirring. The solution of GO and ascorbic acid was then ultrasonicated for 6 hours. The water bath of the ultrasonicator was periodically changed to maintain the temperature of the water at room temperature. The progressive colour change of the GO solution is depicted in Figure 5-14. The GO used was from the Tour method (the reason why this GO was used is explained in Section 5.5 as well as in Chapter 7). The solution was homogeneously black in colour after 90 minutes as seen in Figure 5-14 (d). Barely any further colour change was discernible after this time. The solution was then filtered, and the vacuum filter remained on for an hour to facilitate drying of the solid.

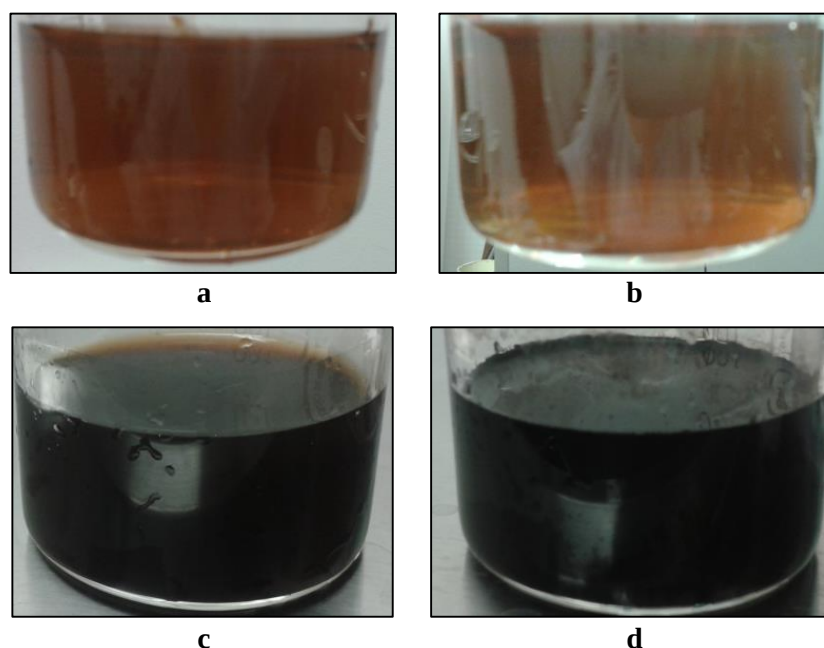


Figure 5-14 GO solution from the Tour method (a); GO solution after addition of ascorbic acid (b); solution after 30 minutes ultrasonication (c); and solution after 90 minutes ultrasonication (d).

5.4.3. Reduction via thermal treatment

The last method of reducing GO was through thermal treatment at elevated temperatures ($> 900\text{ }^{\circ}\text{C}$) [146]. While the previous two reduction methods involved the use of chemicals to achieve reduction, a nonchemical route was investigated to determine its efficiency when compared to the chemical routes. It was found by Wu *et al.* [146] that thermal treatment is in fact more effective at reducing GO than the chemical routes. The GO is placed in a high temperature furnace and subjected to temperatures of $\sim 1000\text{ }^{\circ}\text{C}$ which induces thermal exfoliation and reduction [70]. The layers of individual sheets constituting the GO are separated through the pressure of the Argon gas which is developed between the layers as a result of the high temperature [235]. It has been reported that the electronic properties of the graphene are significantly restored, however, the conductivity of the material does suffer considerably as a result of the defects introduced using this method of reduction [70].

A box was designed to house the GO flakes while in the furnace to protect the sample from contamination during heating (Figure 5-15). The box was made from a single sheet of molybdenum because this metal has an extremely high melting point of 2617 °C [236]. The method for reducing the GO via thermal treatment was then as follows: a film of GO was produced by sonicating 0.5 g of GO (produced via the modified Hummers' method with additional KMnO_4) in ~ 50 ml of distilled water for 30 minutes and filtering the solution using a nylon membrane filter (the reason why this GO was used is explained in Section 5.5 as well as in Chapter 7). The obtained GO film was placed within the box which was then placed within the vacuum furnace. The box and its contents were heated at a rate of 300 °C per hour up to 1000 °C at which it was maintained for approximately 1 hour. The flow rate of the Argon gas was 4.8 L/hr. The furnace was then switched off and the GO contained within its housing was allowed to cool down naturally to room temperature within the furnace overnight. The GO film before and after thermal treatment is depicted in Figure 5-16. The GO films shrink as a result of their exposure to the heat. The obtained reduced material is far lighter and more crinkled in appearance than the GO films, as expected. The reduced films were grey in colour as opposed to the brown GO films (Figure 5-16) and the mass of the films decreased following reduction.



Figure 5-15 Molybdenum box to house the GO samples in the furnace.

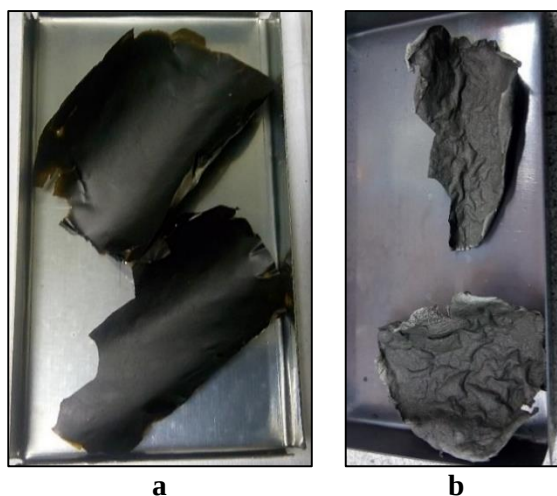


Figure 5-16 GO films before (a) and after (b) thermal treatment.

The Energy-Dispersive X-Ray Spectroscopy (EDX) of the graphene using the SEM produced following the method as detailed above revealed that there was a significant amount of oxygen remaining in the sample which indicated that a large proportion of functional groups had not been removed (this is discussed in greater detail in Chapter 7). This is the result of the relatively short time at which the GO was subjected to a 1000 °C environment thereby resulting in insufficient deoxygenation of the sample. This may also be a result of the environment within the furnace which may not have been completely oxygen-free. When the time at 1000 °C was increased to 3 hours and GO film was broken into smaller flakes to facilitate heating of the material. A reduction of the oxygen content was achieved. This is discussed in Chapter 7.

5.5. Qualitative analysis of synthesised graphene oxide

For qualitative comparison purposes, GO solutions were prepared by dispersing the GO from each of the five experiments in distilled water. In order to prepare these solutions, 0.02 g of each GO was dispersed in 10 ml of distilled water, ultrasonicated for 30 minutes, stirred and thereafter ultrasonicated for another 30 minutes. This resulted in a solution having a GO concentration of 2 mg/ml. The ultrasonication aided in the dispersion of the GO in the water so that a yellow-brown colour could be observed. Prior to dilution, all the GO solutions, except the GO from the Huang method experiment, exhibited a discernible, slightly yellow-brown colour. However, upon stirring of the solutions, a silvery, metallic sediment was observed in four out of the five samples with the exception being that of the solution prepared using GO from the Tour method. This sediment was most likely the un-oxidised, or insufficiently oxidised, graphite. The sediment was only observed upon stirring since the unreacted graphite is denser than the GO, therefore it sinks to the bottom and is more easily seen when stirred. The silvery, metallic sheen of the sediment was consistent with the appearance of graphite itself and therefore may qualitatively validate this assumption. The presence of this sediment was also what obscured the yellow-brown colour of the four solutions thereby giving the solutions a green-brown appearance.

Each GO sample was stirred to ensure a uniform distribution of the GO before syringing out 2 ml of the solution and diluting this in 10 ml of distilled water to attain a solution having an approximate GO concentration of 0.4 mg/ml. Hereafter, the solutions prepared from the GO from each of the five experiments shall be named as follows: GO-1, GO-2, GO-3, GO-4 and GO-5 which indicates the solutions prepared using the GO from: the Hummer's method (GO-1), the modified Hummers' method with extended oxidation time (GO-2), the modified Hummers' method with additional KMnO_4 (GO-3), the Tour method (GO-4) and the Huang method (GO-5), respectively. These solutions are depicted in Figure 5-17. GO-1, GO-3 and GO-4 were clearly yellow-brown while GO-2 was slightly yellow but mostly grey, and GO-5 was grey with a barely discernible hint of yellow. GO-1 and GO-2 had a significant amount of solid present which

quickly settled to the bottom of the vials upon standing. This solid sediment was most likely insufficiently oxidised graphite, as was also apparent in the undiluted solutions. GO-3 also had some solid present however the amount thereof was far less than that observed for GO-1 and GO-2 which indicated that there was possibly a higher conversion efficiency from graphite to GO for this method [230] when compared to the previous two methods. GO-4 did not have any visible solid present however some solid material was visible upon swirling of the vial though this material remained suspended in solution and did not settle to the bottom of the vial upon standing. This solid did not appear black or silvery in colour therefore it was most likely GO which had been oxidised to a lesser extent [230]. There was very little solid present in GO-5 as well. The solution was similar to GO-4 in this respect, however GO-5 was far more grey than yellow – this indicated that the GO present in this solution was oxidised to a lesser extent due to the lack of an obvious yellow-brown colour [230].

If the quality of the GO produced is based purely on the colour of the solutions then the “best” solutions would be GO-4, as the obvious first choice, followed by GO-1. However, the amount of solid present in GO-1 was far more than that present in GO-3. This solution also exhibits an obvious yellow-brown appearance thus indicating that the conversion efficiency from graphite to GO is higher for the modified Hummers’ method with additional KMnO_4 than for the traditional Hummers’ method. Therefore, qualitatively, the two methods which result in GO of the highest quality are the modified Hummers’ method with additional KMnO_4 and the Tour method. This result shall later be confirmed with other characterization techniques such as electron microscopy and X-ray diffraction (XRD) in Chapter 7.

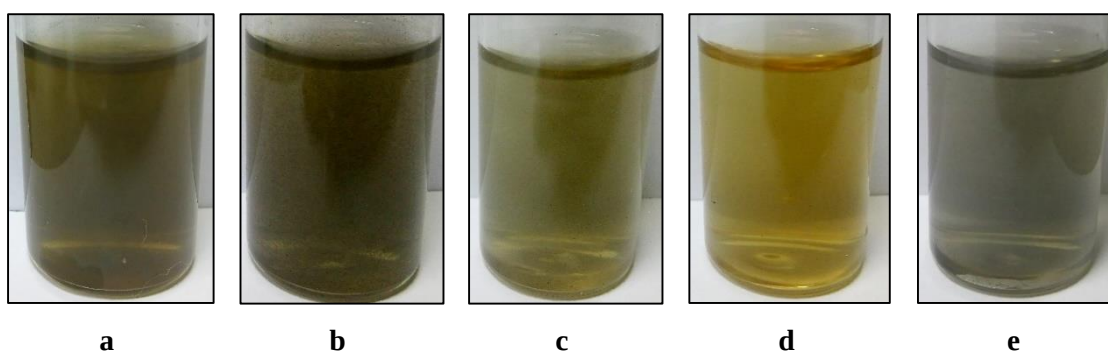


Figure 5-17 GO solutions prepared using the GO from: (a) the Hummer’s method, (b) the modified Hummers’ method with extended oxidation time, (c) the modified Hummers’ method with additional KMnO_4 , (d) the Tour method and (e) the Huang method.

5.6. Summary

Graphene oxide was synthesised using five different experimental methods which each made use of the chemical oxidation of graphite to form GO. Each of the five experimental methods made use of the same quantity of graphite so as to standardise the experiments and enable the results to be compared. The investigated methods were largely similar in the reagents that

were used and the experimental procedures were relatively simple to follow. The first three methods required a comparable amount of experimental time while the fourth method involved a slightly simpler oxidation process. The fifth method required far less physical experimental time since the oxidation reaction was allowed to react to completion over a period of three days at room temperature. However, this method proved to be less safe than the other four methods to execute since a highly energetic, explosive reaction took place while conducting this experiment. The reason for this was that this experimental procedure did not require any form of temperature control, unlike the other four methods. Although this could still be done. The oxidation reactions are exothermic reactions therefore in the absence of an ice bath, the temperature of the reaction would have risen excessively and caused the explosive reaction during the addition of the acid to the KMnO_4 and graphite. The qualitative analysis of the GO produced from each of the five investigated methods suggested that the two methods which produced GO of the highest quality were that of the third and fourth experiments which were the modified Hummers' method with additional KMnO_4 and the Tour method respectively. The qualitative analysis also indicated that the conversion efficiency from graphite to GO of these two methods was the highest thereby suggesting that these methods are the most efficient at producing GO.

Chapter 6 Fabrication of graphene fibres

The secondary aim of this research was to prepare and study the morphology of graphene fibres fabricated through the use of the synthesised graphene together with the chosen polymer material, polyvinyl alcohol (PVA). The graphene fibres were produced on a microscopic scale via the process of electrospinning. Note that the term “graphene fibres” is in fact here a shortened form for graphene/PVA composite fibres. The fibres produced were visible under electron microscopy inspection and the average diameter of the fibres was in the order of 100 nm. The purpose of this stage of the research was to determine a viable method through which to produce graphene fibres. The microscopic production of the graphene nanofibres involved the electrospinning of graphene together with a polymer material. The polymer materials that were investigated were PVA and polystyrene. This would pave the way for further research to be conducted with the focus on investigating and tailoring the properties of the produced graphene fibres for specific applications. Note that due to the iterative nature of the process of optimising the electrospinning parameters, select SEM images have been included in this chapter to aid the reader in following the process that was followed which has been detailed in this chapter. The details of the SEM used may be found in Section 7.1.

6.1. The electrospinning apparatus

As previously mentioned, the electrospinning apparatus comprises three major components: DC high voltage power supply, delivery system and collector. A half wave rectifier high voltage (HV) power supply was designed for the electrospinning experiments to convert alternating input current to direct output current. This power supply was capable of providing an HV output of 0 – 30 kV. A standard half wave rectifier circuit was designed in which the AC input was fed into a step up transformer (220V: 64 kV). The resulting increased voltage was then passed to the forward biased diode D_1 which was used to provide a single phase supply across the output terminals. A smoothing capacitor of 10 nF was used to filter the output to obtain a constant DC output. The resulting HV DC power supply was monitored and varied using an HV probe. The HV DC output voltage of the power supply was ideal for electrospinning since the range of

voltages used for electrospinning falls within this range [182, 192, 203]. The circuit diagram of the designed DC high voltage power supply is seen in Figure 6-1.

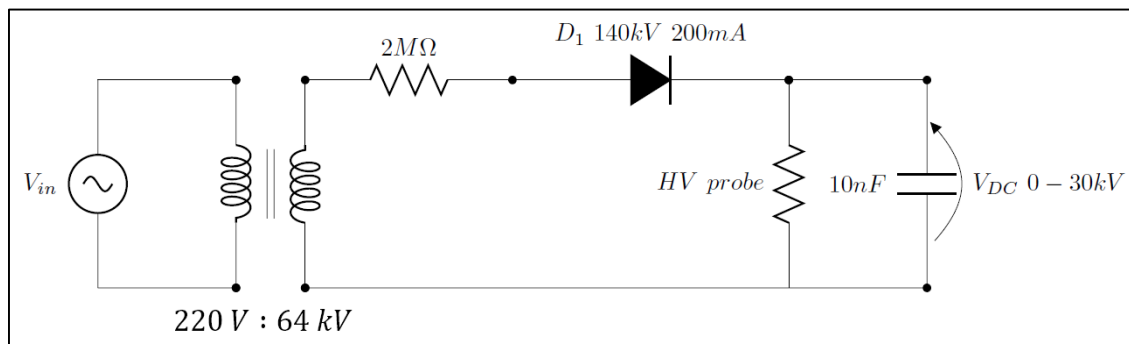


Figure 6-1 Circuit diagram of the designed DC high voltage power supply.

The delivery system made use of a syringe pump which allowed for the controlled dispensing of the solution. The syringe pump may be seen below in Figure 6-2. The pump, a New Era NE-1000 Syringe Pump, holds a single syringe of up to 60 ml and is capable of providing a flow rate of 0.73 $\mu\text{L/hr}$ – 2100 ml/hr. A plastic syringe was used together with this pump, and a disposable, standard bevel needle was attached to the end of this syringe via plastic tubing. The plastic tubing was necessary so that the needle could be positioned inside the Perspex housing within which the electrospinning experiments were executed. The needle/tubing interface was sealed to prevent leakage of the solution. This was tested using water, and all possible breaches were sealed. The needle was connected to the ground of the high voltage power supply through the use of a crocodile clip. The needle was connected to the ground terminal rather than the conventional positive terminal of the high voltage power supply for convenience of the assembly. However, as mentioned, this configuration may also be used.



Figure 6-2 The NE-1000 syringe pump used for electrospinning.

The electrospinning of the various solutions was carried out inside a designed Perspex housing, which is shown in Figure 6-3. Perspex was used since it is a highly durable and transparent material thereby allowing observation of the experiment. A copper conducting

collector plate was secured within the housing at one end. A cable was attached to this plate to allow for the connection to the positive terminal of the high voltage power supply. This can be seen in Figure 6-3 and Figure 6-4 below. A movable stage, as seen in Figure 6-3 (b), was designed with a rubberised edge around its circumference to allow the stage to be easily moved while also fastening the stage once the desired tip-to-collector distance has been achieved. The exterior of the housing was clearly marked so that the tip-to-collector distance could be simply determined. A narrow hole was drilled through the centre of the stage through which the needle could enter the enclosed space. This hole is visible in Figure 6-3 (b) in the centre of the stage. In addition, a few larger holes were drilled into the sides of the housing through which a connector cable could pass and be attached to the needle at various tip-to-collector distances. The design of the electrospinning housing was such that it allowed for the experiments to be performed in the horizontal or vertical configurations. The assembled apparatus is depicted in Figure 6-4, the cable seen in the bottom right of the image was for the attachment to the power supply.

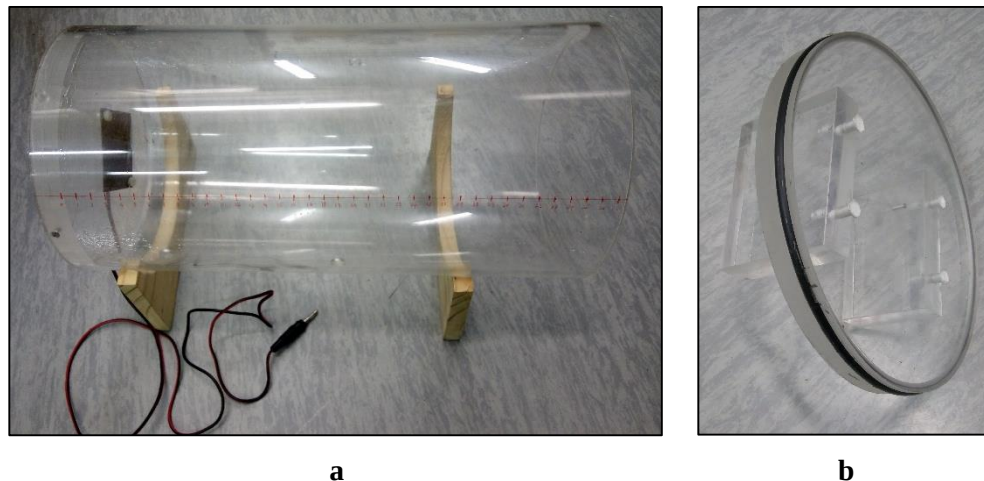


Figure 6-3 Designed Perspex housing (a) and movable stage (b).

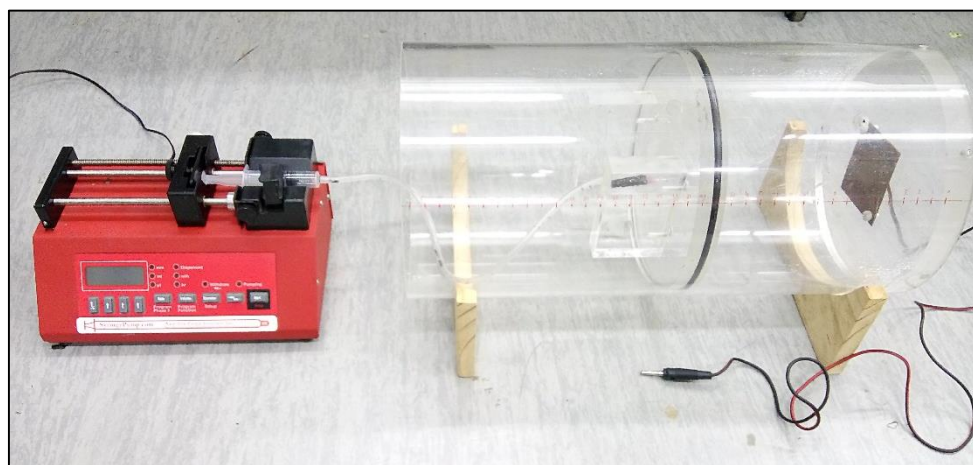


Figure 6-4 Assembled apparatus for electrospinning.

6.2. The high voltage DC power supply

The circuit diagram of the high voltage DC power supply has been provided in the section above and the design thereof may be found in Appendix A. Prior to the initial testing of the electrospinning apparatus in its entirety, the high voltage power supply was tested independently. Thereafter, the electrospinning apparatus was tested together with the power supply. The purpose of this was to test each component of the electrospinning apparatus in isolation in order to ensure that each part operated as designed to meet the conditions required for electrospinning to occur.

6.3. Initial testing for electrospinning

The electrospinning apparatus for the initial testing was assembled in the horizontal configuration. The tubing was filled with ~5 ml of the relevant solution for each experiment and the syringe pump was used to dispense the solution. The collector of the designed electrospinning apparatus was covered in aluminium foil. This foil was removed and replaced with a new piece after each successive experiment to facilitate the collection of the electrospun fibres.

The purpose of the experiments presented in this section was to test the designed electrospinning apparatus in its entirety to ensure that the apparatus met the conditions required for electrospinning. The parameters used for this initial testing have been summarised in Table 6-1. Note that the water and graphene solution was prepared using graphene from previous experiments as detailed in Chapter 5.

Table 6-1 Parameters used for initial testing of electrospinning apparatus.

Material	Needle gauge (G)	Flow rate ($\mu\text{l}/\text{min}$)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)
Water	18	60	5	20	12
Water & graphene	18	30	5	25	12

Water

At 20 kV the droplets were no longer present at the end of the needle and spraying began.

Water & graphene

At 25 kV the droplets shrunk which indicated that electrospinning was occurring. The presence of the graphene in the solution appeared to repel the droplets faster from the tip of the needle to the collector. This could not be attributed to the flow rate as the rate was decreased from the first experiment. Therefore, this apparent increase in the rate of electrospinning was attributed to the presence of the graphene. This experiment indicated that the graphene suspended in the water could have increased the conductivity of the electrospun solution thereby allowing it to be

repelled from the needle at a faster rate. Hence, this preliminary experiment revealed promising findings in that the conductivity of the material appeared to increase with the addition of graphene.

Observations

Both experiments conducted during this initial testing phase indicated that electrospinning had occurred successfully. In the first experiment, the water droplets were no longer present at 20 kV. This indicated that the droplets were being drawn into a fine spray via the process of electrospinning. In the second an increased rate of repulsion was observed when graphene was added to the electrospinning solution. These experiments served to verify that the electrospinning apparatus operated successfully. The second experiment in this testing phase indicated that graphene appears to increase the conductivity of the electrospun material.

6.4. Electrospinning trial

Preparation of PVA aqueous solution

The PVA used was 99 % hydrolysed, sourced from Sigma Aldrich. The process as presented in [191] was initially used to prepare the PVA solution. This process involved mixing the PVA powder in distilled water and thereafter heating to 60 °C to dissolve the PVA. Pirzada *et al.* [191] used this method to produce a 7 % (wt. /vol.) PVA solution using 88 % hydrolysed PVA however the method was adjusted so as to prepare a less concentrated PVA solution. Although, this proved unsuccessful. The difficulty in dissolving the PVA was due to the hydrolysis of the PVA used [237]. Pirzada *et al.* [191] had reported that the PVA dissolved in distilled water at 60 °C however the PVA used was only 88 % hydrolysed whereas the PVA used in this experiment was 99 % hydrolysed. The solubility of 99 % hydrolysed PVA can be compared to a step function: it is very low below 70 °C however it dissolves readily in water above 70 °C [194]. The process was then refined, as outlined below, which resulted in the production of a clear homogenous PVA solution.

The distilled water of 50.0 ml was heated to 80 °C, thereafter 1.00 g of PVA was added in small increments under constant stirring with each addition being dissolved completely before a further addition. Once all the PVA had been dissolved, the heat was reduced and the solution was left stirring until cooled to room temperature. This resulted in a clear, homogenous solution having a concentration of 2 % (wt. /vol.) of PVA in water.

Preparation of GO

The GO used was synthesised using the Modified Hummers' method with additional potassium permanganate (KMnO₄). The GO from this method was used since it was determined to be one of the two methods which produced GO of the highest quality. This was qualitatively

discussed in the previous chapter in Section 5.5 and is further elaborated upon in Chapter 7. GO of 0.2 g was dissolved in ~100 ml of distilled water and sonicated for 30 minutes.

Preparation of graphene

The GO used was synthesised using the Modified Hummers' method with additional KMnO_4 . GO weighing 0.2 g was dissolved in ~100 ml of distilled water and sonicated for 30 minutes. The GO solution was then reduced following the method as described in Section 5.4.1. The reaction appeared to commence immediately upon the addition of the NaBH_4 since rapid bubbling was observed, and the solution turned black after a few seconds [74, 230]. Following this, the solution was sonicated for 30 minutes.

Electrospinning of PVA with GO and graphene

The electrospinning apparatus for the second electrospinning trial was also assembled in the horizontal configuration. For these experiments, 2 ml of the 2 % (wt. / vol.) PVA solution was used together with 1 – 2 ml of either graphene oxide or graphene, depending on the desired concentration. The experiments conducted in this section are summarised in the table below which shows the parameters used for each experiment.

Table 6-2 Parameters used for the electrospinning trial experiment.

Material	Needle gauge (G)	Flow rate ($\mu\text{l}/\text{min}$)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)	Time (mins)
PVA [2 %]	18	30	5	22	10	2
PVA [2 %] : GO (2:1)	18	30	5	22	10	2
PVA [2 %] : GO (2:1)	18	30	5	22	13	2
PVA [2 %] : GO (1:1)	18	30	5	22	13	2
PVA [2 %] : GO (1:2)	18	30	5	22	13	2
PVA [2 %] : G (1:1)	18	30	5	22	13	3

PVA [2 %]

The electrospinning of the 2 % (wt. /vol.) PVA solution successfully produced fibres. The SEM images of these fibres are presented below. As can be seen, the fibres are very fine, however, there was beading present on the strands. The beading may have been caused by the applied voltage being too high [169]. Also, the deposits were not consistent. This suggested that the electrospinning jet was unstable.

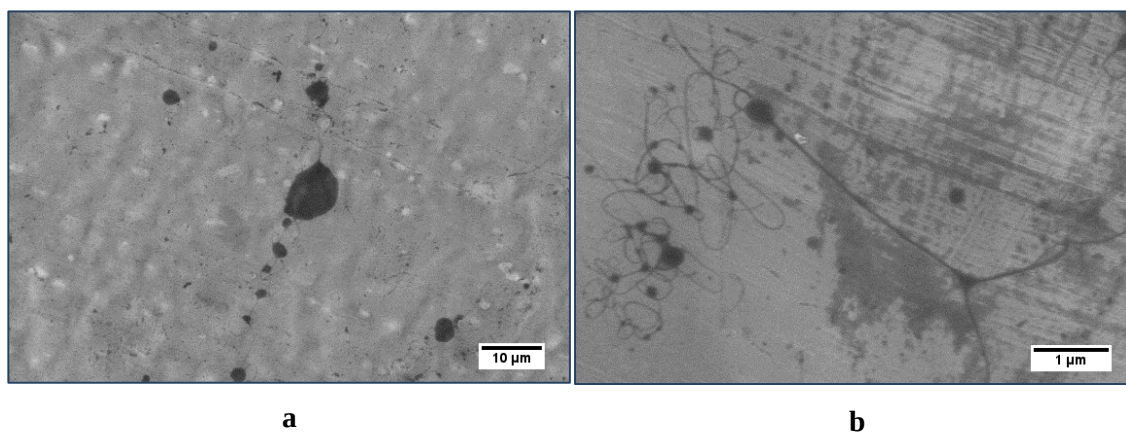


Figure 6-5 SEM images of electrospun fibres produced from the 2 % (wt. /vol.) PVA solution at low magnification (a) and high magnification (b).

PVA [2 %]: GO

Following the SEM analysis of each of the four experiments involving the presence of GO, it was seen that no fibres were produced. Large deposits were present as seen in Figure 6-6. However, even at high magnification no fibres were observed. The SEM images of the other PVA and GO electrospinning experiments that were conducted appeared largely similar to that of Figure 6-6 in that blob-like deposits were observed with no connecting threads.

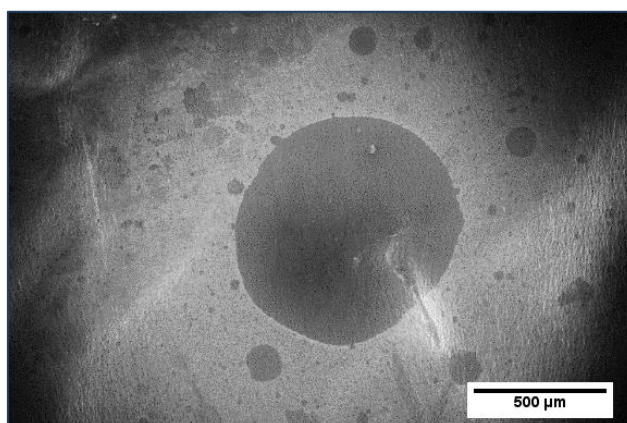


Figure 6-6 SEM image of large deposits produced from the electrospinning of PVA (2 %) : GO (2:1).

PVA [2 %]: G (1:1)

The solution of PVA and graphene in a 1:1 ratio appeared to be expelled outward more noticeably than the previous samples. This could be attributed to the high conductivity of the graphene. There appeared to be an almost uniform deposit present on the sample however when the magnification was increased, there was no evidence of fibres present, as seen in the figure below.

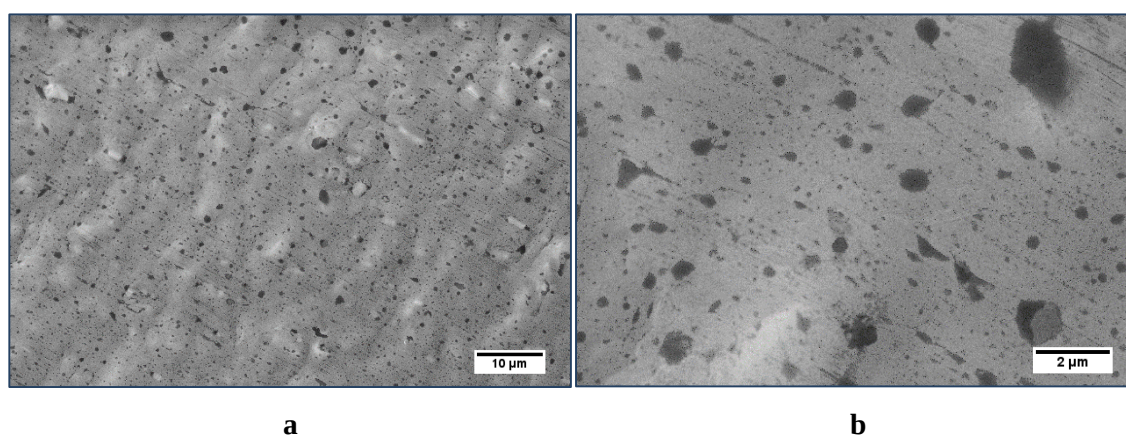


Figure 6-7 SEM images of deposit of electrospun PVA [2%]: graphene (1:1) at low magnification (a) and high magnification (b).

Observations

During the SEM analysis of the samples, it was observed that the electron beam appeared to damage the samples since they were not gold coated. It was decided to coat the samples in gold in the future to prevent damage of the samples. Following analysis of the SEM images obtained from these experiments, it was observed that the fibres produced using a ratio of 1:2 (PVA: GO) did not produce fibres. The reason for this was that the solution was not viscous enough [192, 195, 205]. The GO that was added had been suspended in distilled water therefore upon addition to the PVA solution, unintended dilution of the polymer solution occurred resulting in a less viscous solution. A solution having a viscosity that is too low results in discontinuous fibre production [169]. This observation suggested that a 1:1 or 2:1 ratio (PVA: GO or G) should be used. Furthermore, the absence of fibres could indicate that the PVA concentration of the solution itself was too low thereby resulting in a solution of very low viscosity.

6.5. Preliminary electrospinning trial of PVA and graphene

Preparation of PVA solutions

PVA aqueous solutions of various concentrations were prepared for electrospinning in order to determine the optimum concentration with which to electrospin the graphene fibres. The table below depicts the amount of PVA and distilled water that was used to produce PVA solutions of 4, 6 and 10 % (wt. / vol.).

Table 6-3 Materials used for the preparation of 4, 6 and 10 % (wt. /vol.) PVA solutions.

PVA (g)	Distilled water (ml)	PVA Concentration (% wt. /vol.)
2.00	50.0	4.0
3.03	50.0	6.1
5.01	50.0	10.0

When the graphene suspended in distilled water (from the previous experiment) was added to the 4 % and 6 % PVA aqueous solutions, the solution became a gel almost immediately after the introduction of the graphene to the solution. The gel-like solution was heated to no avail as this only served to turn the gel into a slime. The cause of this gelation was at first unclear; however, after further testing the cause was identified as the presence of residual NaBH_4 in the graphene sample that was added to the PVA solution. This conclusion was reached since when the NaBH_4 was added in isolation to the PVA solution, the liquid congealed after rapid bubbling was observed. This bubbling was similar to that observed during the reduction reactions involving GO and NaBH_4 . This compound reacts with water and since the solvent in the PVA solution was in fact distilled water, the NaBH_4 reacted unfavourably with it thus resulting in the gel formation.

Electrospinning of PVA and graphene – Horizontal configuration

The electrospinning apparatus for the electrospinning of the PVA and graphene solutions was assembled in the horizontal configuration. The experiments conducted in this section are summarised in the table below which shows the parameters used for each experiment.

Table 6-4 Parameters used for the preliminary electrospinning trial of PVA and graphene.

Experiment no.	Material	Needle (G)	Flow rate ($\mu\text{l}/\text{min}$)	Syringe size (ml)	Voltage (kV)	Tip- to- collector distance (cm)	Time (mins)
I	PVA [4 %] : G (2:1)	18	30	5	22	13	3
II	PVA [4 %] : G (1:1)	18	30	5	22	13	3
III	PVA [6 %] : G (2:1)	18	30	5	22	13	3
IV	PVA [6 %] : G (1:1)	18	30	5	22	13	3
V	PVA [10 %] : G (2:1)	18	30	5	22	13	3
VI	PVA [10 %] : G (1:1)	18	30	5	22	13	3

Experiments I – V

The SEM images of the samples produced from each of these five experiments revealed that no fibres had been produced. The results from Experiment I and III were largely similar with the Experiment III revealing more fibre-like deposits however actual fibres were still absent. All the other experiments displayed similar findings of fairly consistent deposits yet no actual fibres.

Experiment VI

All the previous experiments from this particular set of experiments failed to produce fibres except for the last experiment involving a solution of 10 % (wt. /vol.) PVA: G (1:1). The SEM images of this sample revealed chain-like structures of fibres. There was beading present on these fibres, however, the primary feature of interest was the presence of the fibrous material.

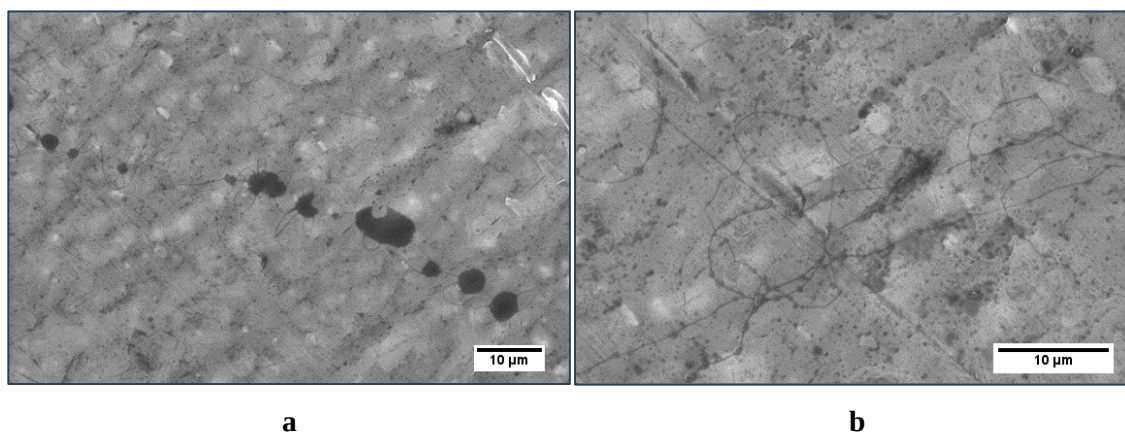


Figure 6-8 SEM images of fibres produced from the electrospinning of PVA [10 %]: G (1:1) at low magnification (a) and higher magnification of the same area (b).

Observations

The concentration of the graphene present in the solutions was determined on a volumetric basis; i.e.: 1 or 2 ml of graphene suspended in distilled water was added to 2 ml of each of the PVA solutions to obtain the desired concentration. This method was unreliable as it introduced unwanted distilled water to the solution. An improvement upon this method was to determine the concentration of the graphene present in the solutions by mass instead. The graphene in the proceeding experiments was dried prior to addition to the PVA solution thereby avoiding dilution of the PVA solution.

In addition, when the samples were initially coated in gold to avoid sample damage, the deposits were not visible under the SEM therefore gold coating of the samples proved to be counterproductive. Thus, an electron beam of lower voltage was instead used when viewing samples from the following experiments to prevent damage to the sample.

The results from this set of experiments were largely inconclusive as fibres were only present in the sample from Experiment VI. This could be caused by the low viscosity of the solutions as mentioned above [206, 207]. The only conclusion which could be reached at this point was that PVA solutions of high concentrations, 10 % (wt. /vol.) and possibly higher, appear to produce fibres. Below this point, no fibre formation was observed, therefore this appeared to be close to the critical solution concentration. However, as mentioned above, this concentration was not the true reflection of the concentration of the solution since distilled water was introduced to the solution with the addition of the graphene which would have diluted the solution somewhat. It was thus concluded that the logical approach was to optimise the electrospinning processing and solution properties for the PVA solutions in isolation prior to the introduction of the graphene to the solutions.

6.6. Electrospinning of PVA

Preparation of PVA aqueous solutions

PVA aqueous solutions of various concentrations were prepared for electrospinning once again. PVA solutions of higher concentrations were synthesised in addition to the existing 4, 6 and 10 % (wt. /vol.) solutions as the solutions of increasing concentration proved to produce higher quality fibres. The literature supports this observation [206, 207]. The objective of this particular experiment was to electrospin PVA solutions of varying concentrations, from the fairly low concentration of 4 % (wt. /vol.) to the very high concentration of 20 % (wt. /vol.). This provided a range of experimental data so as to make an informed choice with regards to the solution with which to create the graphene fibres. The table below shows the amount of PVA and distilled water that was used to produce PVA solutions of 12 and 20 % (wt. / vol.).

Table 6-5 Materials used for the preparation of 12 and 20 % (wt. /vol.) PVA solutions.

PVA (g)	Distilled water (ml)	PVA Concentration (% wt. /vol.)
6.01	50.0	12.0
10.10	50.0	20.2

The 20 % (wt. /vol.) PVA solution was discarded as it was not suitable for electrospinning. The resulting solution after cooling to room temperature was highly viscous and appeared gel-like. These conditions are not appropriate for electrospinning as the surface tension of the liquid would be far too high [169] and would not be easily dispensed using a syringe. Zhang *et al.* [192] suggested that ethanol may be added to a concentrated PVA solution to reduce the viscosity, however, when this was attempted, the solution congealed, as a result, it was discarded.

Electrospinning of PVA solutions – Vertical configuration

The electrospinning apparatus for the electrospinning of the PVA solutions was assembled in the vertical configuration. In this configuration, the force of gravity would aid in the spinning process since the drops would fall from the needle tip towards the collector as a consequence of the vertical configuration. When the samples were collected after electrospinning, the foil was lifted on one end while any unspun solution was allowed to drip off the foil at the other end and the dry, top end of the foil was marked. For SEM analysis, foil samples were taken from the middle of the upper, dry area of the foil to minimise the presence of any unspun solution on the sample. The presence of the unspun solution was a consequence of the vertical configuration of the apparatus. The experiments conducted in this section are summarised in the table below which shows the parameters used for each experiment.

Table 6-6 Parameters used for the electrospinning of PVA.

Material	Needle gauge (G)	Flow rate ($\mu\text{l}/\text{min}$)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)	Time (mins)
PVA [4 %]	18	90	5	20	8	2
PVA [4 %]	18	90	5	22	10	2
PVA [6 %]	18	180	5	22	10	2
PVA [6 %]	18	180	5	22	3	2
PVA [6 %]	18	180	5	22	15	2
PVA [6 %]	18	90	5	22	15	2
PVA [10 %]	18	90	5	22	15	2
PVA [12 %]	18	90	5	22	15	2

PVA [4 %]

This experiment resulted in the successful formation of fibres, although, beading was observed on these fibres. This result disproves the tentative conclusion that was made following the previous set of experiments. The 10 % (wt. /vol.) PVA solution was not the critical solution concentration as fibre formation resulted from the electrospinning of 4 % (wt. /vol.) PVA solution. The differences between the first and second experiments were the voltage and the tip-to-collector distance. The fibres produced from each of these experiments are depicted in the images below. The most noticeable difference between the images of Figure 6-9 and Figure 6-10 shown below at similar magnifications is the density of deposited fibres. This apparent difference was a result of the combination of the two parameters which were changed. The tip-to-collector distance was the most likely primary cause for this difference as more fibres will be deposited at a shorter distance. The similarities between the two figures is the evidence of beading on the fibres shown in all the images and the evidence of fibre formation at fairly low magnifications. As mentioned previously, beading was caused by the applied voltage being too high [169].

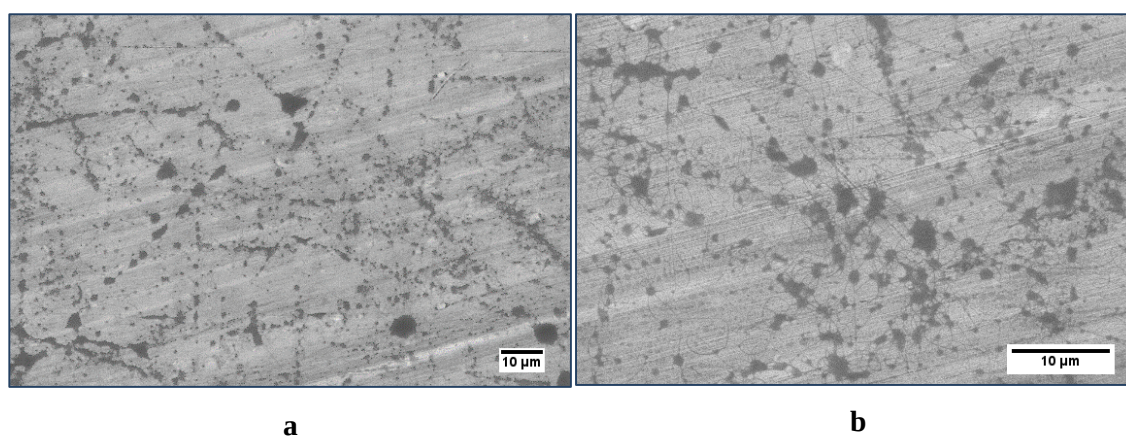


Figure 6-9 SEM images of fibres produced from the electrospinning of 4 % (wt. /vol.) PVA at 20 kV and 8 cm at low magnification (a) and high magnification of the same area (b).

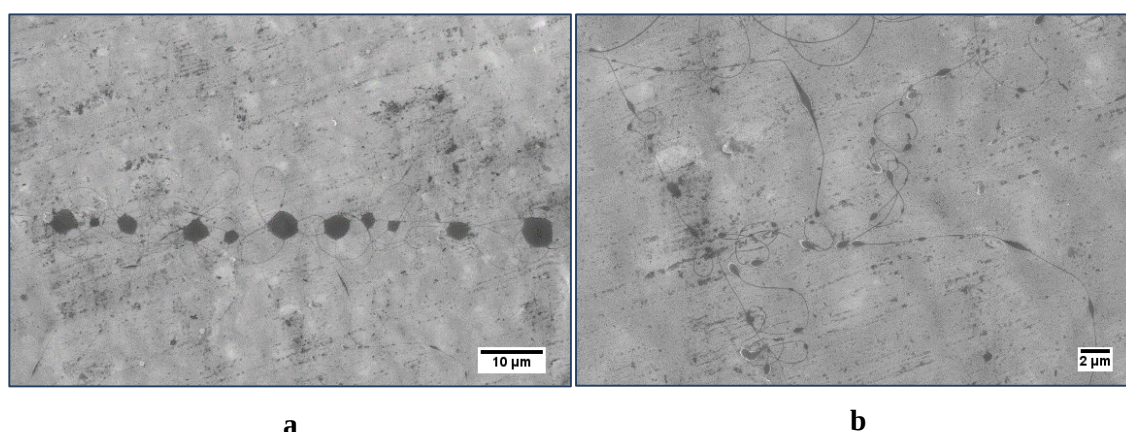


Figure 6-10 SEM images of fibres produced from the electrospinning of 4 % (wt. /vol.) PVA at 22 kV and 10 cm at low magnification (a) and high magnification of the same area (b).

PVA [6 %]

Four electrospinning experiments were carried out using the 6 % (wt. /vol.) PVA solution. The two parameters that were varied between experiments were the flow rate and the tip-to-collector distance. The results from the first experiment showed no evidence of fibres amidst the observed deposit. The absence of fibres in this experiment could be due to the distance from the collector being too large [169]. The fourth experiment displayed similar results with occasional fibres present. The tip-to-collector distance was greater in this experiment which indicated that this could also be a cause for the absence of fibres. Also the flow rate had been halved and in some cases when the flow rate is too low, the Taylor cone may recede into the needle itself resulting in an unstable jet and poor fibre formation [170].

The second and third experiments both showed obvious evidence of fibres. In both of these experiments, all parameters besides the tip-to-collector distance were held constant. The second experiment displayed evidence of extremely large deposits as seen in the SEM images of Figure 6-11. The tip-to-collector distance was decreased to 3 cm at which point a corona was present. This was the shortest distance at which safe operation of the electrospinning apparatus was ensured. These large deposits were caused by the very small tip-to-collector distance which resulted in the fibres not having enough time to dry before reaching the collector [203]. In addition, the fibres produced from the second experiment had large beads present on the strands. This was also attributed to the short tip-to-collector distance [169, 203, 217, 218]. The fibres produced from the third experiment were much finer and the beading was still present, however, it was less prevalent. This can be seen in Figure 6-12. Increasing the tip-to-collector distance reduced the size of the deposits and resulted in fibre production of a higher quality.

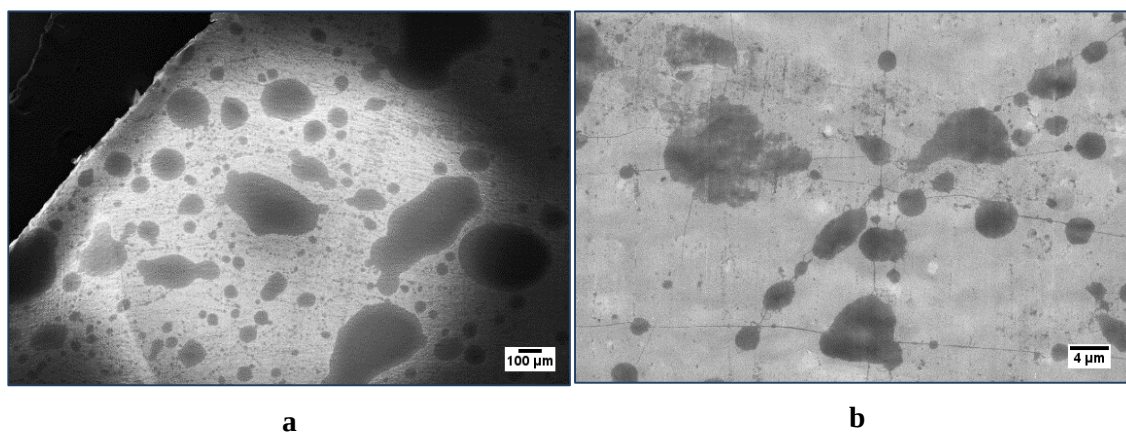


Figure 6-11 SEM images of fibres produced from the electrospinning of 6 % (wt. /vol.) PVA at 180 $\mu\text{l}/\text{min}$ and 3 cm at low magnification (a) and high magnification of the same area (b).

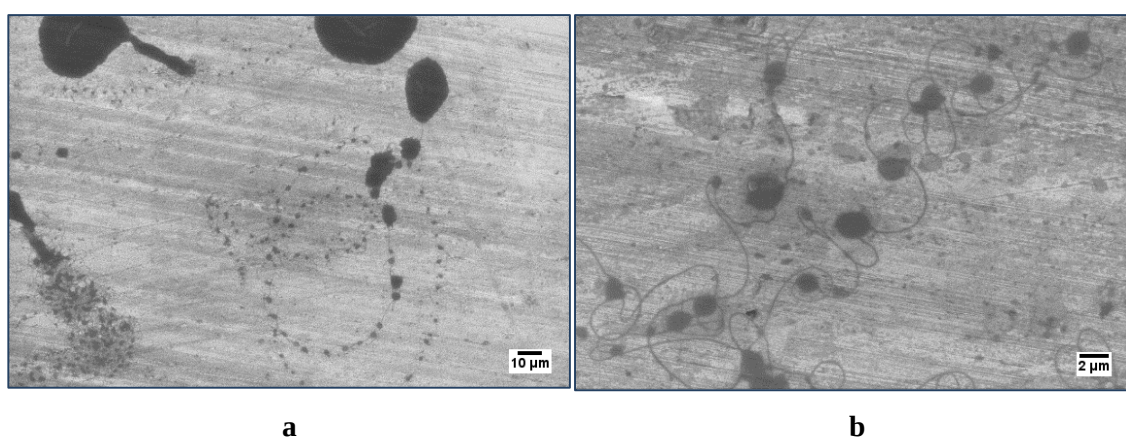


Figure 6-12 SEM images of fibres produced from the electrospinning of 6 % (wt. /vol.) PVA at 180 $\mu\text{l}/\text{min}$ and 15 cm at low magnification (a) and high magnification of the same area (b).

The results from this set of experiments suggest that the tip-to-collector distance influences the prevalence and size of beading on the electrospun fibres. A very high degree of beading was observed when using a tip-to-collector distance of 3 cm, however, the prevalence and size of the beads were greatly reduced when this distance was increased to 15 cm. It also appeared that the flow rate is a significant determining factor on the successful formation of fibres. This was apparent when the third and fourth experiments were compared. A decrease in the flow rate with the tip-to-collector distance held constant resulted in minimal fibre formation.

PVA [10 %]

The product of electrospinning the 10 % (wt. /vol.) PVA solution was a network of fibres. These fibres were web-like as seen in Figure 6-13. This appearance of the fibres could be caused by the flow rate being too high [170, 203]. The foil on which the fibres were collected displayed a visible cloudy frosting. SEM imaging showed that the fibres were densely deposited in a network. The fibre diameter was also wider than in the previous experiments. The average diameter of the fibres produced using the 6 % (wt. /vol.) PVA solution was 92 nm, as compared

to 237 nm for the 10 % (wt. /vol.) solution. When compared to the last electrospinning experiment conducted using the 6 % (wt. /vol.) solution, the only parameter that was altered was the concentration of the solution, however the fibre production greatly improved. Therefore, it was deduced that an increase in the solution concentration influences the morphology and density of the fibres produced [169]. The concentration of 10 % is close to the optimal concentration for the production of high quality electrospun fibres from a PVA solution.

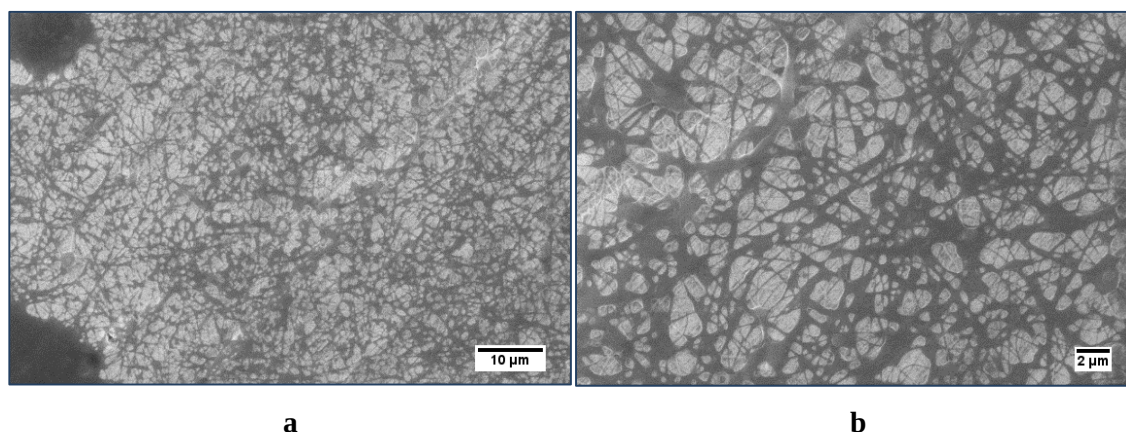


Figure 6-13 SEM images of fibres produced from the electrospinning of 10 % (wt. /vol.) PVA at 90 µl/min and 15 cm at low magnification (a) and high magnification of the same area (b).

PVA [12 %]

The results of the 12 % (wt. /vol.) PVA solution was similar to that of the 10 % solution as a network of fibres was also observed at low magnifications. However, the fibres produced from this solution were more thread-like than web-like as seen in Figure 6-14. This is the desired morphology of the fibres. The fibre diameter was smaller than that observed from the 10 % experiment as a consequence of the increased viscosity of the solution. It was concluded that the 12 % (wt. /vol.) was the optimal PVA solution concentration for the production of high quality electrospun fibres.

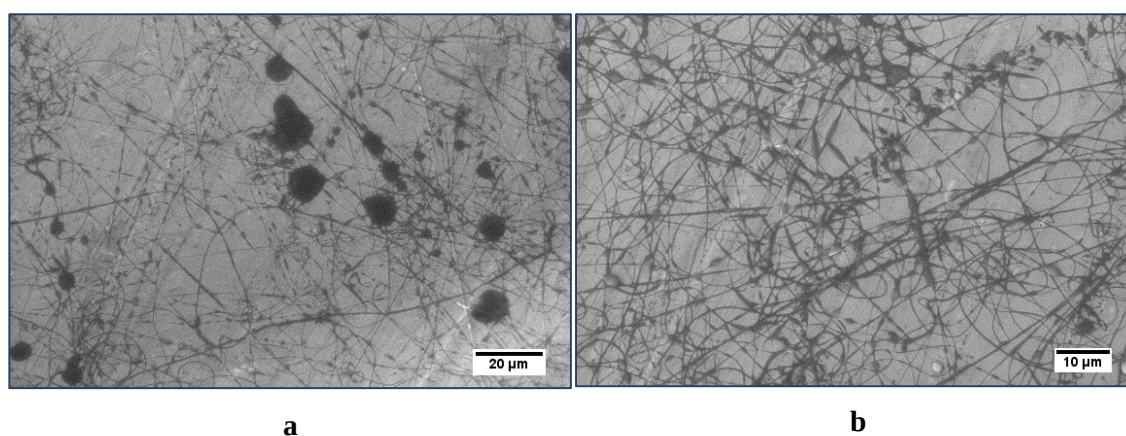


Figure 6-14 SEM images of fibres produced from the electrospinning of 12 % (wt. /vol.) PVA at 90 µl/min and 15 cm at low magnification (a) and high magnification of the same area (b).

Observations

During this experiment, the flashover point was investigated by decreasing the tip-to-collector distance to 3 cm and the voltage was increased to 30 kV. At this point an audible corona was present. Due to safety considerations, the tip-to-collector distance was not decreased any further nor was the high voltage supply increased past 30 kV to prevent flashover from occurring. Therefore, the exact flashover point was not determined. However, for safe operation of the electrospinning apparatus, the upper and lower bounds of the high voltage supply and the tip-to-collector distance was determined to be 30 kV and 3 cm respectively.

During the SEM characterisation of the fibres produced from this experimental trial, it was observed that the PVA solutions of 10 and 12 % (wt. /vol.) produced the highest quality fibres. Therefore, these PVA solutions were used in the following experiments. An increase in the solution concentration produced more prevalent fibres with less beading and the produced fibres exhibited a higher uniformity of diameter. It was also observed that the size and prevalence of beading on the electrospun fibres decreased with a greater tip-to-collector distance. This distance affected the area of deposition of the fibres as well since a very short tip-to-collector distance resulted in a larger area of deposition when compared to that resulting from a greater distance. Furthermore, it was also noted that a significant decrease in the flow rate of the solution resulted in minimal fibre formation.

6.7. Electrospinning trial of PVA and graphene

Many difficulties were initially encountered when attempting to electrospin PVA with graphene. After a number of attempts, the process was eventually refined. However, each attempt has been documented with the purpose of detailing this iterative process. In addition, this will simplify future work related to this research as this chapter of this dissertation may serve as an electrospinning guide to build upon for prospective interested parties.

Trial I – Effect of PVA solution concentration

Synthesis of graphene

Graphene was synthesised by dissolving 1.50 g of GO (synthesised previously using the Modified Hummers' method with additional KMnO_4) in ~100 ml of distilled water. This solution was then ultrasonicated for 15 minutes. The GO solution was reduced by sodium borohydride, as described in Section 5.4.1. Another ~100 ml of distilled water was added to the solution to wash any residual NaBH_4 out from the solution. This solution was then filtered using a vacuum filter. After the filtering of the solution, the rotary pump of the vacuum filter was left running for ~3 hours to facilitate drying of the graphene. Following this, the graphene was removed from the membrane filter and further dried on a hot plate at ~100 °C for 20 minutes. The resulting graphene

flakes were crushed using a mortar and pestle to reduce particle size. The resulting mass of graphene powder was 0.22 g.

Synthesis of PVA solutions

PVA solutions of 10 and 12 % (wt. /vol.) were produced for this experiment. Table 6-7 shows the amount of PVA and distilled water that were used to produce PVA solutions of 10 and 12 % (wt. / vol.).

Table 6-7 Materials used for the preparation of 10 and 12 % (wt. /vol.) PVA solutions.

PVA (g)	Distilled water (ml)	PVA Concentration (% wt. /vol.)
5.01	50.0	10.0
6.01	50.0	12.0

Preparation of solutions for electrospinning

The objective of this experiment was to electrospin PVA with graphene. Therefore, the powdered graphene was added to the PVA solutions prior to electrospinning. The amount of graphene added to each solution is shown in the table below along with the resulting concentration of graphene to PVA.

Table 6-8 Amount of graphene added to PVA solutions and resulting graphene concentration.

PVA solution		Graphene (g)	Graphene concentration (% wt. /vol.)
Concentration (% wt. /vol.)	Amount (ml)		
10	3	0.09	3
12	3	0.09	3

Observations

Once the graphene powder was added to the PVA solutions, the solutions became gel-like and unsuitable for electrospinning after a few minutes as the solution proved difficult to pass through the needle used for electrospinning. This gelation was attributed to residual NaBH_4 present in the graphene powder. Distilled water was used to wash the residual NaBH_4 out as stated previously. However, after the addition of the powder to the PVA solution, it was evident that the NaBH_4 did not dissolve in the water and therefore did not pass through the filter and instead remained present in the graphene sample. Thus, alternative routes were explored through which to remove the NaBH_4 from the sample. Since NaBH_4 dissolves in both methanol and ethanol [238]. The graphene solution was washed with ethanol following the initial filtration with distilled water in the proceeding experiments. This would serve the dual purpose of removing any NaBH_4 present in the sample and would also facilitate drying of the sample.

Another possible cause for the gelation of the solution is that PVA solutions containing water as the solvent age over time and may form gels. Therefore, other possible solvents were explored such as dimethylformamide (DMF). However, this chemical is hazardous and has been

classified as acutely toxic if inhaled or if contact is made with exposed skin [239]. In addition to this, it may cause eye irritation as well as reproductive toxicity [239]. The high voltage power supply that was used for the electrospinning experiments was very large in size and therefore could not be housed in a fume cupboard. As a result, the electrospinning experiments were conducted in the High Voltage Laboratory which is not well ventilated. Therefore, if the DMF were used as the solvent for the PVA solution, the risk of exposure to this chemical would be great hence DMF was rejected as a possible solvent. Other solutions to the gelation problem were explored, such as synthesising a fresh batch of PVA solutions for each experiment.

The third possible cause for the difficulty of the PVA/graphene solution to pass through the needle used for electrospinning is that the needle could have become blocked. It was observed upon addition of the graphene to the PVA solution that some of the graphene had aggregated. And the aggregate would have prevented the solution from passing through the fine needle tip. This was addressed in the next experiment by ultrasonicated the PVA/graphene solution for a longer period of time to ensure that the graphene in the solution would not aggregate to pass through the needle tip.

Trial II - Effect of PVA solution concentration and flow rate

Synthesis of graphene

The graphene used for this experiment was synthesised using a similar method as that of the previous experimental trial however 0.50 g of NaBH_4 was used to reduce 1.50 g of GO (synthesised previously using the Modified Hummers' method with additional KMnO_4). Less NaBH_4 was added to the GO in this experiment since the previous trial indicated that this chemical caused the gelation of the PVA/graphene solutions. Therefore, it was attempted to minimise its presence in the solution. The reaction appeared to be as vigorous as the previous experimental trial, and a black mixture was produced with the reduced amount of NaBH_4 – this qualitatively indicated that reduction of GO was achieved [74, 230].

Another ~100 ml of water was added to the solution, which was then filtered. To facilitate drying of the solid, the rotary pump was left on for ~1 hour. Following this, the solid was scraped off the membrane filters and washed with ~30 ml of ethanol. As stated previously, the ethanol dissolves NaBH_4 which will then pass through the filter. The solution was then ultrasonicated for 15 minutes. This sonication served the purpose of reducing the size of the graphene flakes. After sonication, the solution was filtered once again. The solid appeared sufficiently dry after leaving the vacuum pump on for ~1 hour, and it was easily peeled off the membrane filter. The resulting mass of graphene after the second filtration with ethanol was 0.16 g. Lastly, the graphene was crushed using a mortar and pestle.

Preparation of solutions for electrospinning

The PVA solutions of 10 and 12 % (wt. /vol.) synthesised for the previous experiment were used again. This experiment was carried out 5 days after the previous trial, therefore the solutions would not have aged significantly. The powdered graphene was added to the PVA solutions prior to electrospinning. The amount of graphene added to each solution is shown in the Table 6-9 together with the resulting concentration of graphene to PVA.

Table 6-9 Amount of graphene added to PVA solutions and resulting graphene concentration.

PVA solution		Graphene (g)	Graphene concentration (% wt. /vol.)
Concentration (% wt. /vol.)	Amount (ml)		
10	3	0.08	2.7 $\approx$ 3
12	3	0.08	2.7 $\approx$ 3

Following the addition of the graphene to the PVA solutions, each solution was ultrasonicated for 4 hours. This sonication served to homogenise the PVA solution and to reduce the size of the powdered graphene to ensure that it did not hinder the flow of the solution through the needle during electrospinning.

Electrospinning of PVA and graphene solution

For this electrospinning experiment, the apparatus was also assembled in the vertical configuration. The solutions that were electrospun along with the corresponding parameters are presented Table 6-10 below.

Table 6-10 Parameters used for the electrospinning of PVA and graphene solution.

Material	Needle gauge (G)	Flow rate (μ l/min)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)	Time (mins)
PVA [10 %] & G	18	500	5	20	15	3
PVA [12 %] & G	18	500	5	20	15	3
PVA [12 %] & G	18	1000	10	20	20	3

The flow rate was significantly higher than that used for the previous experiments since difficulties in dispensing the solution were encountered, and it appeared that the solution was not being dispensed through the needle tip. Air seemed to be entering the solution due to inadequate sealing at the needle/tubing interface. In addition, the method which was adopted for the electrospinning experiments which entailed filling the tubing with $\sim$ 5 ml of the relevant solution and using an air bubble to dispense the solution did not prove successful for this experiment. During all three of these experiments, the droplets appeared to be dispensed at an inconsistent rate, and the droplets seemed to fall onto the collector rather than being spun into fibres. The

results from this experimental trial were therefore deemed unreliable as evidence of electrospinning of the solution was absent.

Observations

Although electrospinning of the solutions produced for this experiment proved difficult, two vital observations were made. Firstly, the graphene was successfully added in powder form to the PVA solutions. This indicated that the ethanol wash was successful in removing the residual NaBH_4 . And secondly, the difficulty experienced in electrospinning the solutions proved to be a dispensing rather than a solution problem as air was being drawn into the tubing due to insufficient solution being loaded into the syringe and tubing. This prevented the liquid from being smoothly dispensed. Upon the unsuccessful conclusion of this phase of testing, it was decided to investigate the effect of using an alternative polymer solution on the fibre production in the form of polystyrene dissolved in amyl acetate.

Trial III – Effect of polymer solution

Synthesis of graphene

The graphene used for this experiment was synthesised and cleaned using the identical method used in the Experimental trial II, as described above.

Synthesis of polymer solutions

The 10 and 12 % (wt. /vol.) PVA solutions were used from the previous experiment. In addition, an 8 % (wt. /vol.) PVA solution was synthesised. This solution was synthesised to increase the sample set of PVA solutions so that a greater range of concentrations could be tested for electrospinning. The table below shows the amount of PVA and distilled water that were used to produce an 8 % (wt. / vol.) PVA solution.

Table 6-11 Materials used for the preparation of the 8 % (wt. /vol.) PVA solution.

PVA (g)	Distilled water (ml)	PVA Concentration (% wt. /vol.)
4.01	50.0	8.0

The polystyrene/amyl acetate solutions were synthesised by dissolving polystyrene in amyl acetate. The polystyrene dissolved immediately upon addition to the amyl acetate and formed a slightly cloudy solution that was less viscous than the equivalent PVA solutions. The table below shows the amount of polystyrene and amyl acetate that were used to produce solutions of 8 and 10 % (wt. /wt.).

Table 6-12 Materials used for the preparation of 8 and 10 % (wt. /wt.) polystyrene/amyl acetate solutions.

Polystyrene (g)	Amyl acetate (g)	Polystyrene/amyl acetate concentration (% wt. /wt.)
4.01	49.76	8.06
5.00	49.69	10.06

Preparation of solutions for electrospinning

The powdered graphene was added to the polymer solutions prior to electrospinning. The amount of graphene added to each solution is shown in the Table 6-13 together with the resulting concentration of graphene to polymer solution.

Table 6-13 Amount of graphene added to polymer solutions and resulting graphene concentration.

Polymer solution	Concentration (% wt. /vol.)	Amount (ml)	Graphene (g)	Graphene concentration (% wt. /vol.)
PVA	10	3	0.07	2.33 $\approx$ 2
PVA	12	3	0.07	2.33 $\approx$ 2
Polystyrene/amyl acetate	8	3	0.07	2.33 $\approx$ 2
Polystyrene/amyl acetate	10	3	0.07	2.33 $\approx$ 2

Following the addition of the graphene to the polymer solutions, the solutions were ultrasonicated for 5 hours. This sonication served to homogenise the polymer solutions and to reduce the size of the powdered graphene to ensure that it did not hinder the flow of the solution through the needle during electrospinning. The graphene did not disperse in the PVA solutions, instead it remained suspended towards the surface of the solutions. Yet it dispersed very easily in the polystyrene/amyl acetate solutions. The graphene was removed from the 8 % PVA solution and added to ethanol in an attempt to disperse the graphene in the ethanol under sonication. However, this proved unsuccessful as the residual PVA formed a gel in the ethanol. Therefore, this gel was washed with water and heated to form a less viscous solution. The graphene was added to 3.0 ml of distilled water and sonicated to reduce the size of the graphene. The graphene powder suspended in water was then heated to evaporate most of the water prior to adding this powder to the PVA solutions. This proved successful and avoided the addition of any foreign material to the solution. Also, the concentration of the PVA solutions was negligibly affected as most of the water of the graphene solution had been evaporated.

Electrospinning of solutions

For this electrospinning experiment the apparatus was initially assembled in the vertical configuration and later changed to the horizontal configuration. The configuration was changed since the amyl acetate present in the polystyrene/amyl acetate polymer solution interacted unfavourably with the tubing used to dispense the solution. The experiments conducted in this section are summarised in Table 6-14 which shows the parameters used for each experiment.

Table 6-14 Parameters used for the electrospinning of polymer solutions and graphene.

Material	Needle gauge (G)	Flow rate (µl/min)	Syringe size (ml)	Voltage (kV)	Tip to collector distance (cm)	Time (mins)
Polystyrene/amyl acetate [8 %]	18	120	5	20	15	2
Polystyrene/amyl acetate [8 %] & graphene	18	180	10	20	15	2
Polystyrene/amyl acetate [10 %] & graphene	18	180	10	20	15	2
PVA [8 %] & graphene	18	120	5	25	10	2
PVA [8 %] & graphene	18	70	5	20	5	3
PVA [10 %] & graphene	18	70	5	20	5	3
PVA [12 %] & graphene	18	70	5	20	5	3

Polystyrene/amyl acetate solutions

As mentioned previously, difficulties were experienced when handling the polystyrene/amyl acetate solution. As a result of these difficulties, the flow rate was increased when electrospinning these solutions. The amyl acetate dissolved the tubing used as well as the syringe therefore the syringe was changed to a larger, 10 ml syringe. The tubing was replaced by a new plastic tube of the same length and material. Furthermore, the solution had a strong smell, and after being exposed to this solution for a period of ~1 hour, respiratory discomfort was experienced. This indicated that future experiments using this solvent, should be carried out within a fume cupboard.

The SEM characterisation of deposits from the three experiments involving polystyrene/amyl acetate solution revealed no evidence of fibre production. There also appeared to be several impurities present in the sample. These impurities could have been environmental contaminants. The samples were very beam-sensitive at 20 kV, therefore, these samples were viewed using an acceleration voltage of 5 kV instead. Even at 5 kV beam damage was observed, therefore, new samples were prepared and gold coated. The SEM analysis of the samples revealed deposits but these deposits were not fibrous. The gold coated samples did not reveal any threads connecting the deposits either. The SEM image taken from the sample of the electrospun polystyrene/amyl acetate (8 %) and graphene experiment, as seen in Figure 6-15, revealed that even at magnifications of ~3 000, no fibres were visible.

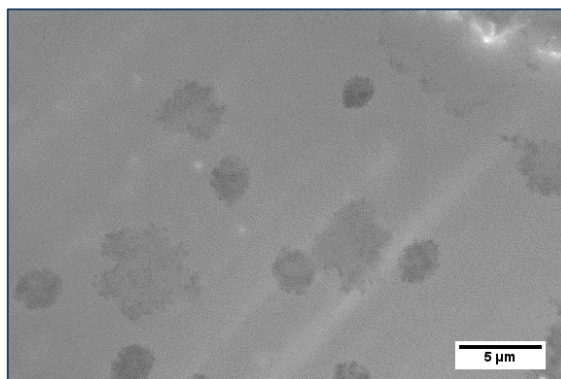


Figure 6-15 SEM image of the gold coated deposit produced from the electrospinning of 8 % (wt./wt.) polystyrene/amyl acetate and graphene.

PVA [8 %] & graphene

The results from the first experiment using the 8 % (wt./vol.) PVA solution with graphene showed that very fine fibres were produced. The diameters of these fibres were much narrower (~ 20 nm) than those produced previously in the PVA electrospinning experiments of Section 6.6. An example of the fibres produced using this solution is shown below.

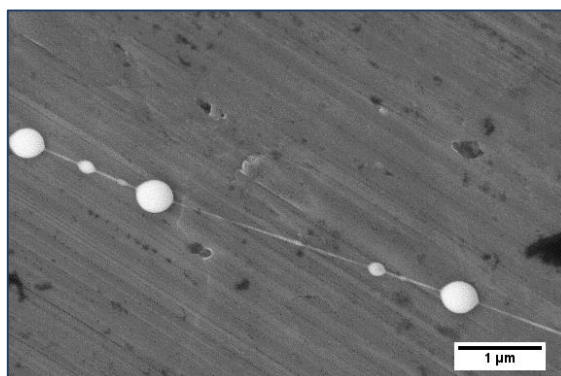


Figure 6-16 SEM image of the fibres produced via the electrospinning of 8 % (wt./vol) PVA solution with graphene.

In a second experiment, the tip-to-collector distance was halved. The SEM image from the second experiment revealed a deposit that was evenly distributed throughout the sample, however, even at magnifications of $\sim 9\,000$, no threads connecting the deposits were visible. SEM images of samples from this experiment can be seen in Figure 6-17 (a) at low magnification and in Figure 6-17 (b) at higher magnification.

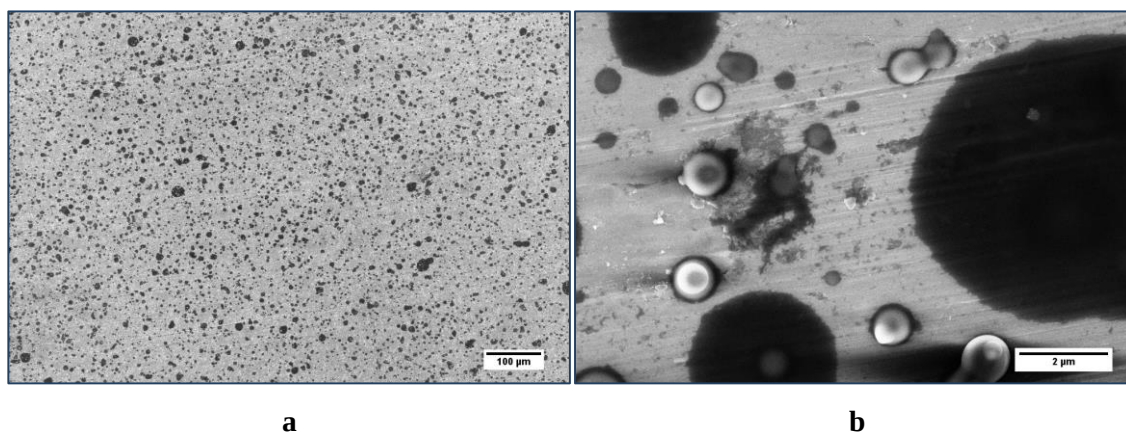


Figure 6-17 SEM image of the deposits produced via the electrospinning of 8 % (wt. /vol) PVA solution with graphene at a tip-to-collector distance of 5 cm.

PVA [10 %] & graphene

The results from this experiment revealed a similar pattern of deposits to the previous experiment although, high magnification of these deposits revealed threads interlinking the beads. The SEM images shown in Figure 6-18, show that significant beading of the fibres occurred, possibly caused by the short tip-to-collector distance of 5 cm [169, 203, 217, 218]. The bright areas depicted in Figure 6-18 (b) are possibly contaminants, while the darker areas are the fibrous deposits.

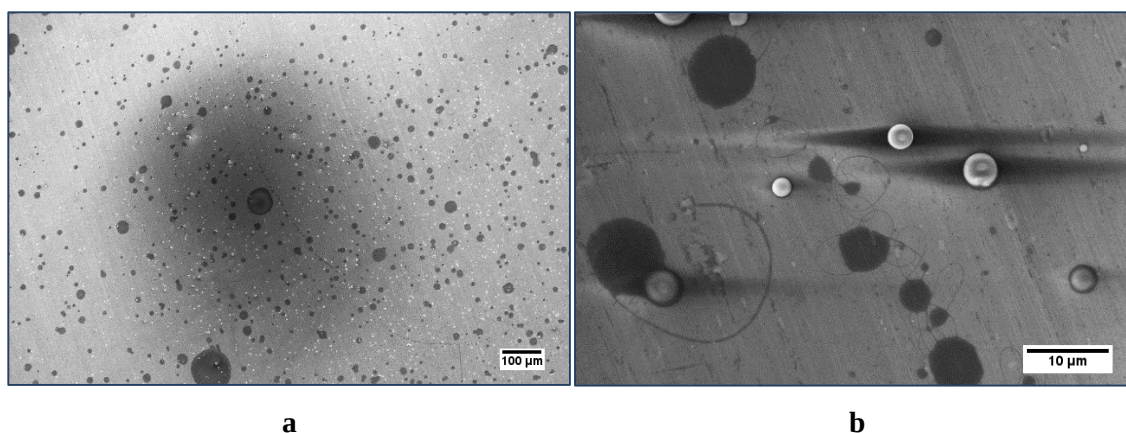


Figure 6-18 SEM images of the fibres produced via the electrospinning of 10 % (wt. /vol) PVA solution with graphene at low magnification (a) and high magnification of the same area (b).

PVA [12 %] & graphene

The results from this experiment appeared to be the most promising. Fibres were visible even at low magnifications as seen in Figure 6-19 (a). In addition, the fibres appeared to have less beading between the threads. This suggests that the electrospinning parameters used for this experiment were close to the optimal point.

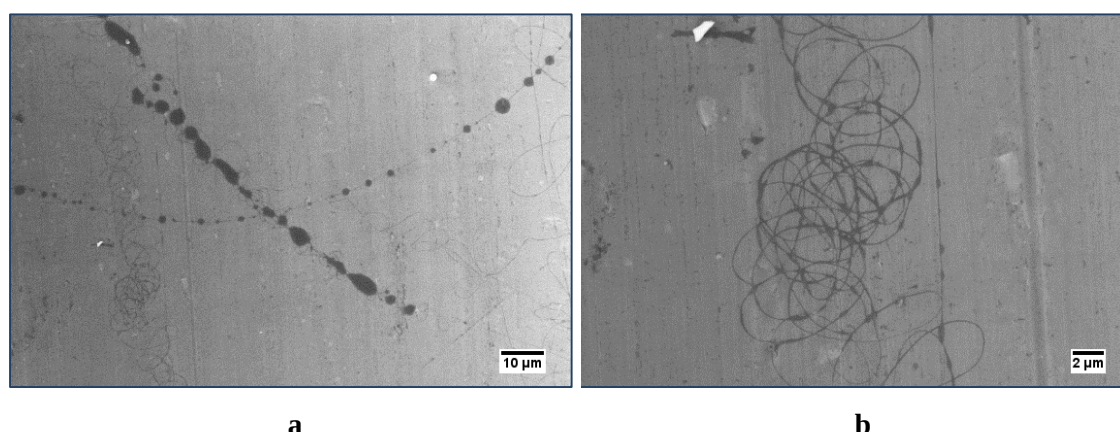


Figure 6-19 SEM images of the fibres produced via the electrospinning of 12 % (wt. /vol) PVA solution with graphene at low magnification (a) and high magnification of the same area (b).

Observations

Based on the test results presented above, the polystyrene/amyl acetate solutions were not tested any further. As mentioned, the amyl acetate present in the solution resulted in respiratory discomfort and since the electrospinning was conducted in the High Voltage Laboratory with limited ventilation, the use of this chemical was not ideal. Furthermore, the solution appeared to interact unfavourably with the tubing and syringes thereby hindering the flow of the solution. The most important consideration when deciding to exclude this polymer solution was the absence of fibre production in all the samples. If the negative effects of using this chemical were to be mitigated, glass syringes would have to be used, and the electrospinning should be conducted in a well-ventilated room or in a fume cupboard. Also, the solution should have a higher concentration of polystyrene or a similar polymer to increase the viscosity and thereby increase the likelihood of fibre production [206, 207].

Following analysis of the SEM image data collected from these experiments, it was concluded that the PVA solutions of 10 and 12 % (wt. /vol.) with graphene produced fibres of the highest quality. The 12 % (wt. /vol.) solution in particular produced fibres of a high quality. These fibres displayed a high degree of uniformity and beading was less prevalent. In addition, it was observed that the addition of the graphene to the solutions changed the optimum processing and solution parameters. Therefore, the optimum solution and processing parameters as determined from the electrospinning of PVA solutions of various concentrations only loosely apply to these solutions.

6.8. Introduction of graphene to PVA for electrospinning

Trial I – Washing via ethanol

Synthesis of graphene

For the synthesis of the graphene used for this experiment, GO from the Tour method was used. The reason for this was that the GO from the modified Hummers' method with additional KMnO_4 was rapidly being depleted, and in an effort to save some of this reagent for other experiments, GO of a similar quality was used. Graphene was synthesised by dissolving 1.50 g of GO (synthesised previously using the Tour method) in ~100 ml of distilled water. This solution was then ultrasonicated for 30 minutes. The beaker containing the solution was then placed in a fume cupboard and 0.50 g of NaBH_4 was added to the solution and left to stir for 15 minutes. However, the NaBH_4 did not seem to react immediately with the solution as observed during previous experiments using GO from the third experiment. Therefore, the solution was left to stir for a further 30 minutes. After this time had elapsed, the solution remained brown in colour thereby indicating that reduction of the GO had not sufficiently occurred [74, 230]. It was assumed that the NaBH_4 that was added was insufficient to reduce the highly oxidised GO produced from the Tour method. Therefore, an additional 0.52 g of NaBH_4 was added to the solution and allowed to stir for 30 minutes. The solution turned black after this time had elapsed thus indicating that sufficient reduction of the GO had occurred [74, 230].

Another ~100 ml of water was added to the solution and filtered. To facilitate drying of the solid, the rotary pump was left on for ~1 hour. Following this, the solid was scraped off the membrane filters. The graphene synthesised using the GO from the Tour method did not appear to peel off the nylon membrane filter as easily as the previously synthesised GO. The resulting graphene was then washed with ~50 ml of ethanol. The solution was then ultrasonicated for 20 minutes. This sonication served the purpose of reducing the size of the graphene flakes. After sonication, the solution was filtered once again. The resulting mass of the graphene after the second filtration with ethanol was 0.15 g. Lastly, the graphene was crushed using a mortar and pestle.

Preparation of solutions for electrospinning

The PVA solution used for this experiment was the 12 % (wt. /vol.) PVA solution that was synthesised for the previous experiments. The graphene was added to 3.0 ml of distilled water and sonicated for 30 minutes. The graphene powder suspended in water was then heated to evaporate most of the water prior to adding this powder to the PVA solutions. However, upon the addition of the graphene to the PVA solution, congealing of the solution occurred.

Observations

When the synthesised graphene was added to the PVA solution, this once again caused the solution to congeal. This indicated that there may have been residual NaBH_4 present in the graphene due to insufficient washing of the solution. It was attempted to remove the NaBH_4 from the graphene (as detailed above), however this was unsuccessful. Another possible cause could be insufficient drying of the graphene prior to its addition to the distilled water. If ethanol traces had still been present in solution, this could have been dissolved in the water and caused the PVA to congeal. Although the GO used for this experiment was synthesised via the Tour method instead, this was not the primary factor responsible for the gelation of the PVA since this was also experienced when using GO synthesised via the modified Hummers' method with additional KMnO_4 and the commonality between the resulting graphene produced was the reducing agent, sodium borohydride.

Trial II – Use of less sodium borohydride (NaBH_4)

Synthesis of graphene

It was attempted to synthesise graphene once again using the method as detailed above for Trial I, but with less NaBH_4 in order to prevent the congealing of the PVA solution. After the first addition of NaBH_4 , the solution was slightly brown after stirring for 15 mins. Therefore, it was left to stir for another 40 minutes after which the mixture appeared black. After this, the solution was ultrasonicated for 15 minutes. Although, when a few millilitres of the solution was dispensed onto the membrane filter it was still slightly brown therefore 0.21 g of NaBH_4 was added to the solution. Less NaBH_4 was added as the presence of this compound was the most likely cause behind the congealing of the solution. The solution was then stirred for 10 minutes and sonicated for another 10 minutes. However, the solution still appeared slightly brown when another attempt to filter the solution was made. Thus, another 0.15 g of NaBH_4 was added to the solution. The solution was stirred and sonicated for 10 minutes each prior to filtration. Upon filtration, the solution finally appeared black in colour thereby indicating that the GO had been reduced [74, 230]. The vacuum filter was left on for an hour to draw out excess water. After this period of time had elapsed, it was noted that bubbles had formed on the surface of the solid. This suggested that the NaBH_4 had not reacted to completion with the GO prior to filtering the solution. After the solid was removed from the membrane filter, it was washed with ~30 ml of ethanol, ultrasonicated and filtered once again. Following the filtering of the graphene in ethanol, the mass of the graphene was 0.38 g. This was then removed from the membrane filter and heated on a hot plate at 90 °C for 10 minutes to remove all traces of the ethanol from the solid. The mass of the graphene after heating was 0.27 g which revealed that there had been residual ethanol present in the material.

Preparation of solutions for electrospinning

The PVA solution used for this experiment was the 12 % (wt. /vol.) PVA solution that was synthesised for the previous experiments. The graphene was added to 3.0 ml of distilled water and sonicated for 30 minutes. The graphene powder suspended in water was then heated to evaporate most of the water prior to adding this powder to the PVA solutions. However, upon the addition of a small amount of the graphene to the PVA solution, congealing of the solution occurred. This indicated that the presence of residual ethanol was not the problem since this had been evaporated when heated. Therefore, the remaining graphene was washed with ethanol, ultrasonicated, filtered and heated once again in order to remove other ethanol-soluble residual salts that may have been present in the material. The same process of sonicating the graphene in distilled water and heating this was followed prior to the second attempt at addition to the PVA solution. However, gelation of the solution resulted once again.

Observations

Following the failed attempt to successfully add the graphene reduced via sodium borohydride to the PVA solution, it was concluded that the factor responsible for the gelation of the PVA was the NaBH_4 itself. The other possible factors that could have led to this result such as the presence of residual ethanol as well as the use of GO synthesised via different methods have been investigated and it was proven that these factors did not cause the gelation. As this chapter has shown thus far, multiple attempts at incorporating graphene reduced via NaBH_4 have been made and out of these many attempts, only one was successful. This led to the decision to explore reducing GO via alternative methods. This is expanded upon in the following section of this chapter.

6.9. Optimisation of the electrospinning of PVA and graphene

As mentioned above, alternative means through which to reduce GO were explored. Specifically, a reducing agent which does not result in the congealing of the PVA solution. This led to the method of reducing GO via ascorbic acid which has been discussed in Section 5.4.2. The experiment presented in this section made use of graphene synthesised via the ascorbic acid method. This experiment forms the conclusion of the experiments conducted to fabricate microscopic graphene fibres possessing an average diameter of ~ 100 nm.

Synthesis of graphene

GO synthesised via the Tour method was used for this experiment. An amount of 1.02 g of GO was dissolved in ~ 100 ml of distilled water and ultrasonicated for 30 minutes. An amount of 1.02 g of the ascorbic acid powder was weighed in and added to the GO solution. The GO was

then reduced following the method as detailed in Section 5.4.2. The solution was filtered and the vacuum filter remained on for an hour to facilitate drying of the solid.

Preparation of solutions for electrospinning

The PVA solution used for this experiment was the 12 % (wt. /vol.) PVA solution that was synthesised for the previous experiments. The synthesised graphene was added to 2.0 ml of distilled water and ultrasonicated for 30 minutes. This solution was heated to evaporate most of the water prior to the introduction of the graphene to the PVA solution. A small amount of graphene was added to a few millilitres of PVA solution. This proved successful as the solution did not congeal. Since the addition of the graphene to the PVA was successful, more graphene was synthesised using this method in order to add a sufficient amount to the PVA solution. Once 1.00 g of graphene had been synthesised, this was divided into two portions of mass 0.50 g each. Each of these graphene samples were added to 10 ml of PVA 12 % (wt. /vol.) solution to attain two composite solutions possessing a graphene concentration of 5 % (wt. /vol.) each.

Electrospinning of solutions

For this electrospinning experiment, the apparatus was assembled in the horizontal configuration to avoid unspun solution falling onto the collector. The parameters which were investigated during this set of experiments were the needle gauge size and the tip-to-collector distance. The solutions that were electrospun along with the corresponding parameters are presented in Table 6-15. The only material which was electrospun was the composite solution of graphene and 12 % (wt. /vol.) PVA solution therefore this parameter has been omitted from the table.

Table 6-15 Parameters used for the electrospinning of 12 % (wt. /vol.) PVA solution and graphene.

Experiment no.	Needle gauge (G)	Flow rate (µl/min)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)	Time (mins)
I	18	70	5	20	5	3
II	18	70	5	20	10	3
III	18	70	5	20	15	3
IV	22	70	5	20	5	3
V	22	70	5	20	10	3
VI	22	70	5	20	15	3

Experiment I

During the experiment, it was observed that the droplets shot forward towards the collector, and droplets were visible on the foil covering the collector. This indicated that the tip-to-collector distance was too short. This manifested in the SEM images in the form of visible deposits at low

magnifications of ~ 100 . The fibres had prevalent, large beads present, as seen in the figure below. This was a result of the short tip-to-collector distance [169, 203, 217, 218].

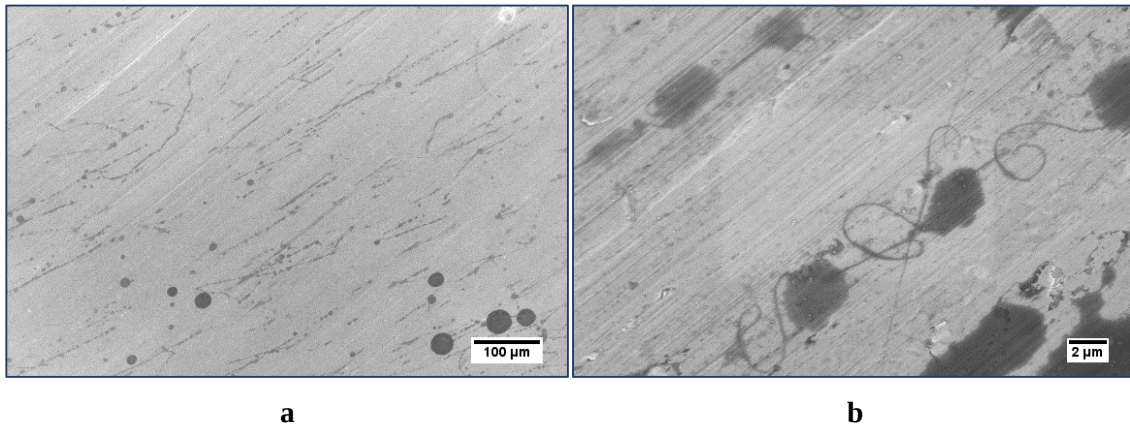


Figure 6-20 SEM images of the fibres produced from Experiment I at low magnification (a) and higher magnification of the same area (b).

Experiment II

For this experiment the droplets also appeared to shoot forward in the direction of the collector, however, no visible droplets were observed on the foil covering the collector itself. This suggested that this tip-to-collector distance was closer to the optimum point. The SEM images (Figure 6-21) revealed a higher amount of deposits than the previous experiment. These deposits were visible at very low magnifications of ~ 30 . The beads present on the fibres decreased in size, and more fine fibres were observed. This is a direct consequence of the larger tip-to-collector distance [203]. This is evident in Figure 6-21 when compared with Figure 6-20.

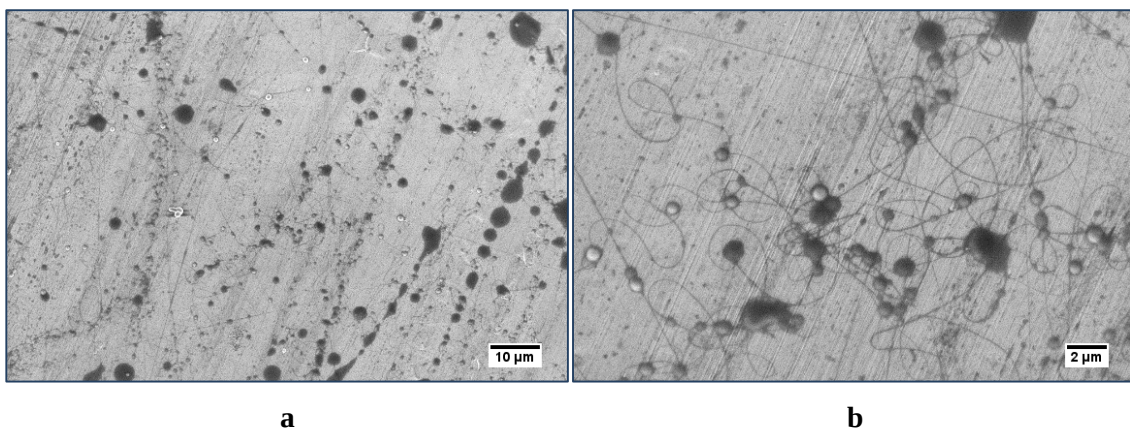


Figure 6-21 SEM images of the fibres produced from Experiment II at low magnification (a) and higher magnification of the same area (b).

Experiment III

The SEM analysis of the fibres fabricated from this experiment also revealed deposits at low magnifications, however, the deposit was in the form of a dense network of fine fibres which was interspersed with occasional large deposits. A higher magnified image of the fibres confirmed

this, as seen in Figure 6-22 (b). Furthermore, the beading present on the fibres was smaller and less prevalent than in the previous two experiments. This indicated that the tip-to-collector distance of 15 cm was closest to the optimum point of electrospinning the graphene/ PVA solution.

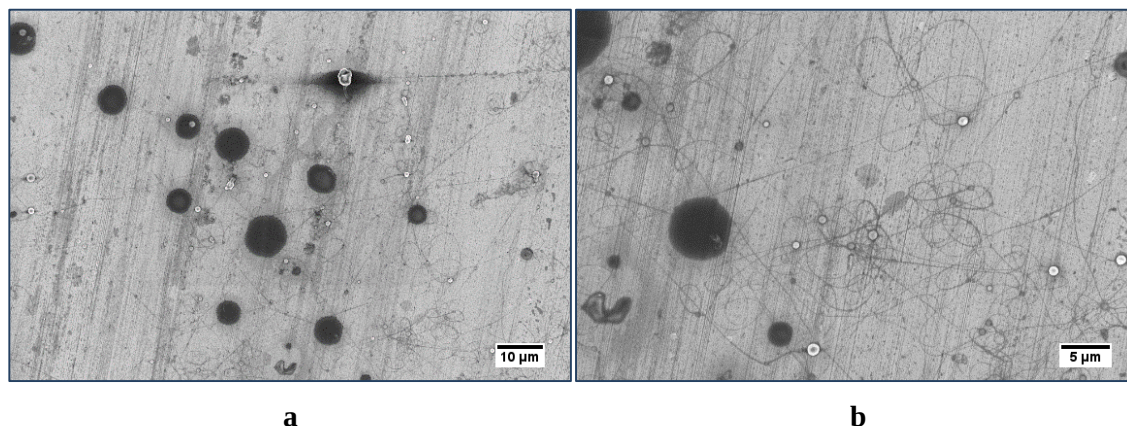


Figure 6-22 SEM images of the fibres produced from Experiment III at low magnification (a) and higher magnification of the same area (b).

Experiments IV – VI

Experiments IV to VI did not yield any electrospun fibres. High magnification (4 000 – 6 000) of these samples revealed deposits of the solution yet no fibres. This lack of fibre formation was a result of the change in needle size as this was the sole parameter which was changed between the first set of experiments (I-III) and this set (IV-VI).

Concluding experiment

Following the conclusion of this set of experiments, the method which produced the most favourable results in terms of the experiments discussed after SEM analysis of the fibre morphology was determined as Experiment III of this section of experiments. The parameters used in this experiment were as follows: PVA solution concentration of 12 % (wt. /vol.), a graphene concentration of 5 % (wt. /vol.), a flow rate of 70 µl/min, an applied voltage of 20 kV and a tip-to-collector distance of 15 cm. The experiment was then repeated however it was kept running for 2 hours with the intention of producing a visible collection of a dense network of fibres upon which conductivity and strength measurements could be performed. However, after 2 hours had elapsed, the deposited fibres were barely discernible by the eye.

Observations

It was initially intended to also make use of the 25 G needle. However, the flow rate seemed to be too low when using the 22 G needle and this parameter served as a constant for this set of experiments therefore it remained unchanged. Also, if the flow rate is too low, this could result in the formation of a Taylor cone which recedes into the needle itself thus forming an unstable jet

which would produce fibres of poor quality [170]. Instead, it was concluded that the 25 G needle was too narrow for the given, fixed parameters. Following the SEM analysis of the samples from Experiments IV – VI it was clear that the 22 G was also too narrow for the given fixed parameters. The effect of the needle size is related to the delivery and flow rate of the solution since needles that are too fine would result in difficulties with dispensing the solution. Thus the fibre formation would suffer as well.

The effect of the tip-to-collector distance was also investigated during this set of experiments and it was found that a larger tip-to-collector distance resulted in finer fibres (average diameter of 107.40 nm) with less prevalent and smaller beads on the strands. This observation is consistent with literature reports [203].

6.10. Discussion of electrospinning experiments

The graphene/PVA solution which was synthesised for the experiments as described in Section 6.9 formed a stable suspension since the graphene still remained uniformly distributed in the PVA solution after several weeks. No agglomeration or settling was observed, which disagrees with the findings of Wang *et al.* [190] where it was reported that graphene does not easily disperse in PVA solution. This uniform suspension can be seen in Figure 6-23.



Figure 6-23 Uniform mixture of graphene suspended in a solution of PVA.

The electrospinning experiments conducted are summarised in Table 6-16 which shows the parameters used for each experiment. The experiments which resulted in the successful production of fibres have been highlighted in light green. In total, 37 electrospinning experiments were carried out, of which only 14 resulted in the formation of fibres. This confirmed that electrospinning needs an iterative approach, and that the adjustment of a single parameter greatly influences the outcome. Optimising these parameters proved to be a laborious yet necessary process to ensure that the fibres produced were of a high standard. These desired characteristics were a high degree of uniformity of the fibres, minimal beading, and average diameters of ~ 100 nm. The optimum parameters determined during these extensive electrospinning trials were as follows: PVA solution concentration of 12 % (wt. /vol.), a graphene concentration of

5 % (wt. /vol.), a flow rate of 70 $\mu\text{l}/\text{min}$, an applied voltage of 20 kV and a tip-to-collector distance of 15 cm. This experiment has been highlighted in a darker shade of green.

Table 6-16 Summary of electrospinning experiments (green: successful attempts, dark green: best outcome and optimum parameters).

	Material	Needle gauge (G)	Flow rate ($\mu\text{l}/\text{min}$)	Syringe size (ml)	Voltage (kV)	Tip-to-collector distance (cm)	Time (mins)
1	Water	18	60	5	20	12	2
2	Water & graphene	18	30	5	25	12	2
3	PVA [2 %]	18	30	5	22	10	2
4	PVA [2 %] : GO (2:1)	18	30	5	22	10	2
5	PVA [2 %] : GO (2:1)	18	30	5	22	13	2
6	PVA [2 %] : GO (1:1)	18	30	5	22	13	2
7	PVA [2 %] : GO (1:2)	18	30	5	22	13	2
8	PVA [2 %] : G (1:1)	18	30	5	22	13	3
9	PVA [4 %] : G (2:1)	18	30	5	22	13	3
10	PVA [4 %] : G (1:1)	18	30	5	22	13	3
11	PVA [6 %] : G (2:1)	18	30	5	22	13	3
12	PVA [6 %] : G (1:1)	18	30	5	22	13	3
13	PVA [10 %] : G (2:1)	18	30	5	22	13	3
14	PVA [10 %] : G (1:1)	18	30	5	22	13	3
15	PVA [4 %]	18	90	5	20	8	2
16	PVA [4 %]	18	90	5	22	10	2
17	PVA [6 %]	18	180	5	22	10	2
18	PVA [6 %]	18	180	5	22	3	2
19	PVA [6 %]	18	180	5	22	15	2
20	PVA [6 %]	18	90	5	22	15	2
21	PVA [10 %]	18	90	5	22	15	2
21	PVA [12 %]	18	90	5	22	15	2
22	PVA [10 %] & G	18	500	5	20	15	3
23	PVA [12 %] & G	18	500	5	20	15	3
24	PVA [12 %] & G	18	1000	10	20	20	3
25	Polystyrene/amyl acetate [8 %]	18	120	5	20	15	2
26	Polystyrene/amyl acetate [8 %] & graphene	18	180	10	20	15	2
27	Polystyrene/amyl acetate [10 %] & graphene	18	180	10	20	15	2
28	PVA [8 %] & graphene	18	120	5	25	10	2
29	PVA [8 %] & graphene	18	70	5	20	5	3
30	PVA [10 %] & graphene	18	70	5	20	5	3
31	PVA [12 %] & graphene	18	70	5	20	5	3
32	PVA [12 %] & graphene	18	70	5	20	5	3
33	PVA [12 %] & graphene	18	70	5	20	10	3
34	PVA [12 %] & graphene	18	70	5	20	15	3
35	PVA [12 %] & graphene	22	70	5	20	5	3
36	PVA [12 %] & graphene	22	70	5	20	10	3
37	PVA [12 %] & graphene	22	70	5	20	15	3

6.11. Summary

The results from the electrospinning experiments are summarised in Table 6-16. These results indicated that only 14 out of the 37 conducted electrospinning experiments resulted in the successful formation of fibres. This confirmed the need for extensive experiments to be conducted in order to optimise the electrospinning parameters. Throughout these experiments, it was noted that the individual parameters have a substantial effect upon the morphology of the fibres. The adjustment of one parameter often influences that of another parameter, such as that observed between the flow rate and applied voltage. Therefore, the parameters should be adjusted systematically, one parameter at a time to avoid unintentional effects upon the various other parameters.

The process is iterative, the optimum parameters determined during the electrospinning trials were as follows: PVA solution concentration of 12 % (wt. /vol.), a graphene concentration of 5 % (wt. /vol.), a flow rate of 70 $\mu\text{l}/\text{min}$, an applied voltage of 20 kV and a tip-to-collector distance of 15 cm. While graphene/PVA composite fibres were successfully electrospun, it proved difficult to produce fibres which were visible to the naked eye and which would therefore be more easily manipulated. However, these graphene/PVA fibres may be used as a strengthening filler in many composite materials as suggested by Liang *et al.* [227] and may also find use in applications such as electrodes, conductive wires, as well as for biomedical applications [193]. From a Materials Science point of view, the average thickness (107.40 nm) of the produced fibres was so fine as to be considered a quasi-one-dimensional material which may, if studied, have interesting physical properties.

Chapter 7 Results and discussion

The products resulting from the five experimental methods investigated for the synthesis of GO in addition to the three explored methods of reducing GO were analysed using SEM, TEM and XRD. The SEM images provided an indication of the surface morphology and indicated the size of the flakes as well as any topological defects present. The TEM images provided insight into the relative thickness of the flakes, confirmed the size thereof and also revealed any contamination present through the use of Energy-Dispersive X-Ray Spectroscopy (EDX). The images collected from the electron microscopy analysis allowed for the various synthesis methods and electrospinning to be compared based on the observed quality of their products. In addition, EDX from SEM was conducted on samples to determine the degree of oxidation as well as the degree of reduction (or deoxygenation). XRD analysis of the samples provided an indication of the crystallinity of the samples and also allowed the resulting patterns to be compared with the expected results from literature to confirm that the various products had in fact been produced. The complementary results of the microscopy and XRD data confirmed the qualitative analysis of the GO experiments.

It is relevant to note here that while an in-depth study was conducted on the characterisation of graphene oxide and graphene through the use of Raman spectroscopy, this method of characterisation is not presented here. Raman analysis of the produced samples was conducted over a period of several weeks using the Raman spectroscope at the UKZN Westville campus, however no reliable spectra were produced. The possible reasons as to why the instrument failed to produce reliable spectra for the various samples were explored and corrected although this was met with no improvement of the data. Therefore, it was decided to opt for XRD analysis instead which proved to be the more reliable diagnostic tool.

In this chapter the GO experiments are referred to by number which corresponds to the various experiments as follows: Experiment 1 – Hummers' method, Experiment 2 – modified Hummers' method with extended oxidation time, Experiment 3 – modified Hummers' method with additional KMnO_4 , Experiment 4 – Tour method, and Experiment 5 – Huang method.

In addition, the nanoscale fibres resulting from the electrospinning of graphene and PVA were analysed using SEM. These images allowed the morphology and size of the fibres to be

studied in order to determine the influence of the various processing parameters on the fibre morphology.

7.1. Instrumentation

The Scanning Electron Microscope utilised was a Carl Zeiss Ultra Plus Field Emission SEM coupled to SmartSEM software. The detector of the SEM is a secondary electron detector. The resulting SEM images are generated from secondary electrons. Energy-Dispersive X-Ray Spectroscopy was performed on the SEM using an Oxford Instruments EDX detector and Aztec software. The software is calibrated with a copper standard and quantification is based on this calibration. The software applies Pulse Pile-Up correction and Matrix correction which is more accurate than ZAF or Phi-Rho-Z corrections. The software also has a built in library of the various elements which is used to match the detected energies to the library references.

The Transmission Electron Microscopes used were a JEOL JEM 2100 TEM operated at an acceleration voltage of 200 kV and a JEOL 1010 TEM operated at 100 kV. The samples for both SEM and TEM analysis were prepared by ultrasonically dispersing a miniscule amount of the sample material in ethanol for approximately 10 minutes. The result is an almost clear solution.

For SEM analysis, a sample holder was covered with carbon tape and a pipette was used to decant a few drops of the solution onto the tape. The samples were then placed under a heated lamp to evaporate the ethanol prior to analysis. In some instances, the samples were gold coated but most of the samples were not gold coated as the coating obscured the sample. The sample holders were placed in a stage that was inserted into the SEM chamber. This allowed the surface of the samples to be scanned.

For the TEM analysis, the sample holder was dipped into the prepared solution using forceps. The sample holder was then placed under a heated lamp to evaporate the ethanol prior to analysis. The sample holder grid consisted of copper with a holey carbon support film on which the samples sit. The carbon film is approximately 18 nm thick. The samples were loaded individually into the TEM chamber and were analysed.

The X-ray diffractometer was a D8 Advance X-ray diffractometer manufactured by Bruker Corporation and the accompanying utilised software was the DIFFRAC.SUITE. GO and graphene films on nylon membrane filters were taken for XRD analysis. The films were removed from the filter and were untreated prior to analysis. The samples were compacted into the sample holder, flattened and analysed. The diffractometer was operated at 40 kV and 40 mA and was equipped with a graphite monochromator and a Vantec detector. The radiation source used was a $\text{CuK}\alpha$ X-ray source with a wavelength, $\lambda = 1.5406 \text{ \AA}$. The data was collected at a step size of 0.014° over a 2θ range from 5° to 70° .

7.2. Results of the synthesis of graphene and graphene oxide

7.2.1. Graphene oxide results

Surface morphology: SEM data

Prior to the presentation of the SEM images resulting from the five GO experiments, the SEM images of the starting, parent material, graphite is provided for comparison purposes. In the images below, graphite's flake-like nature due to the layered structure can be observed. It was difficult to determine an average flake size from these images since there was a wide size distribution, as seen in Figure 7-1 (a). The general appearance of the individual flakes was layered, as seen in Figure 7-1 (b), and as expected.

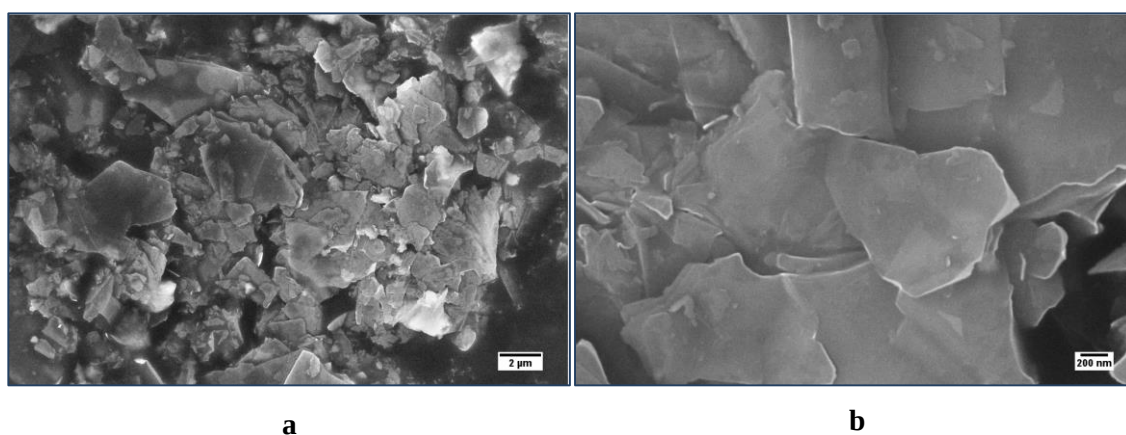


Figure 7-1 SEM images of graphite at low magnification (a) and higher magnification (b).

The SEM images of the products resulting from the five GO experiments are presented below in Figure 7-2. The average diameters of the flakes shown for Experiments 1 – 5 are: 16 μm , 39 μm , 42 μm , 48 μm and 35 μm respectively. Five flakes were measured from each experiment and three measurements were taken per flake. The standard deviations are: 13 μm , 11 μm , 15 μm , 14 μm and 22 μm , respectively for Experiments 1 – 5. The range of flakes sizes for Experiments 1 – 5 is: 3 – 40 μm , 16 – 58 μm , 25 – 87 μm , 27 – 91 μm , and 16 – 78 μm , respectively. The variation in the sizes of the GO flakes is due to the different oxidation mechanisms involved in each of the methods which would likely have affected the particle size. The flake size from Experiment 1 and 5 varied the greatest while the flake size from the other three experiments was more consistent. In addition, ultrasonication was performed on the samples while submerged in ethanol prior to viewing the samples using SEM and TEM. This would possibly have also decreased the flake size and caused variations thereof. It can be seen from the images that Experiments 1 – 4 resulted in GO with a layered appearance, while Experiment 5 produced GO with what appears to be significant topological defects due to the highly crinkled appearance of the GO produced using this method. Higher magnification of the GO sample produced via Experiment 5 revealed similar findings, and the material appeared to consist of multiple layers,

similar to graphite. This observation could be a consequence of the explosive reaction which occurred during the oxidation process for Experiment 5 which could have resulted in a higher degree of unreacted graphitic material. Another difference between this method and the other four is the average size of the flakes which was substantially smaller than that of the other methods. The resulting GO flakes produced from Experiment 5 were not as large as previously reported [102]. This is most likely due to the graphite precursor material used. The graphite used, here, was natural coarse grade graphite with relatively small flake size ($\sim 150\text{ }\mu\text{m}$) while the graphite used by Huang *et al.* [102] had an average flake size of $500\text{ }\mu\text{m}$. As seen in Figure 7-1, the graphite flakes used were far smaller than this. The flakes in Figure 7-1 were also much smaller than $150\text{ }\mu\text{m}$ due to the ultrasonication of the sample in ethanol prior to examining this sample using the SEM. However, the graphite flakes were not ultrasonicated prior to their use in the synthesis experiments, therefore they were closer to their original size of $150\text{ }\mu\text{m}$ during the experimentation. Another likely cause for the small flake size of the GO from Experiment 5 was the crushing of the graphite flakes together with the KMnO_4 crystals to form a fine powder as a precautionary measure for this experiment. This step was not done by Huang *et al.* [102]. The graphite source was not altered for this experiment as it was desired to use this as a control variable in all five experiments. Experiments 2, 3, and 4 resulted in the production of GO which exhibited the desired smooth planar surfaces while low magnification images of GO from Experiment 1 revealed highly rough sheets of GO. Experiment 4 resulted in the production of large-area GO sheets. The other four experiments also produced GO whose appearance was consistent with that presented in the literature. Since SEM is not sufficient to fully characterise GO or graphene due to the 2D nature of these materials, TEM was used to further characterise the materials and their quality in terms of topological defects and morphology.

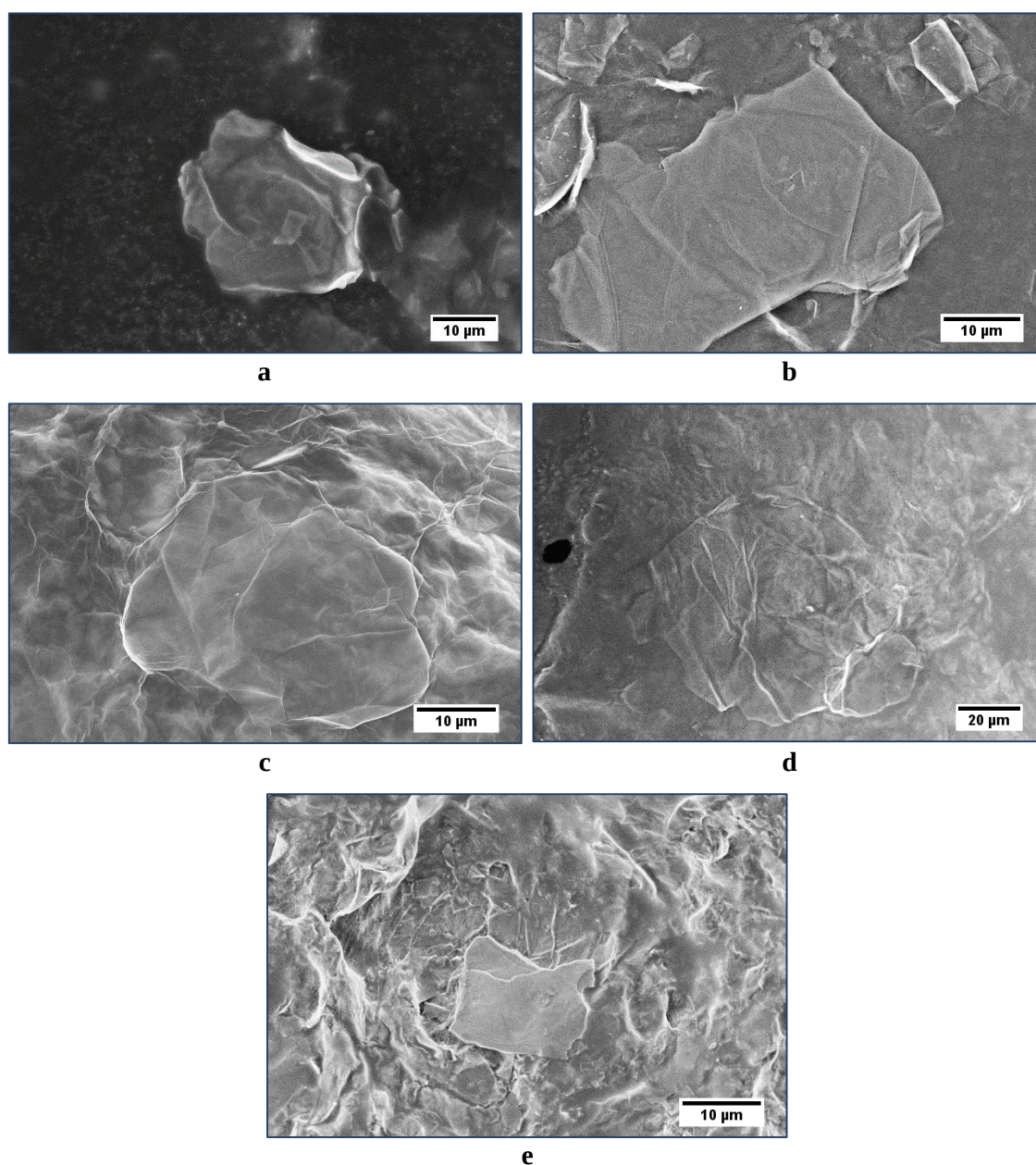


Figure 7-2 SEM images of the GO flakes produced from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively.

2D nature and thickness: TEM data

The TEM images of the five samples of GO revealed a nanoscale material that was similar to experimental results presented in the theory. The observed flakes were of a 2D nature and electron transparent, showing very little contrast. Sonication of the GO samples suspended in ethanol prior to imaging allowed for the individual sheets to be separated, and the results are the images depicted below. The lace-like background of the images is the holey carbon film used to hold the sample for imaging.

The GO samples produced from Experiments 1 and 2 appeared quite similar. The flakes were thin and consisted of a few layers as seen in images a and b of Figure 7-3. Image a indicates that the GO produced via this route resulted in thin, small GO flakes. Image b shows that the GO from Experiment 2 appeared to be slightly thicker than that of Experiment 1. This is indicated by the darker appearance of the flake in some areas. This indicates that there are thicker and thinner areas of the flake. This may indicate actual steps in the material, flakes on top of each other, or simply folded flakes. However, the relative surface area of the flake is comparable to that depicted in image a. The GO flakes produced from Experiment 3 were larger than those of Experiments 1 and 2. Image c depicts multiple sheets stacked together as suggested by its darker appearance. These darker regions may also indicate folded flakes. The GO produced from Experiment 4 was the largest area product out of all five experiments. This can be seen in image d. During the microscopy analysis of this sample, it was difficult to obtain a low magnification image of an individual flake as the low magnification images revealed overlapping sheets of GO. Individual flakes were not observed. The GO obtained from this method was also very thin, as image d shows, since it appears highly electron transparent in this image. Lastly, Experiment 5 also produced larger flakes than the GO from Experiments 1 – 3. It exhibits a layered appearance at similar magnifications while the other GO samples consist of smaller flakes. These sheets of GO appear similar to that of the GO from Experiment 4 since both are highly electron transparent thus suggesting that the material consisted of only a few layers of GO. Although, it should be noted that the images d and e were taken using the TEM that was operated at 100 kV rather than the TEM operated at 200 kV as the microscope was inoperable at the time. Therefore, the sheets may appear slightly less transparent.

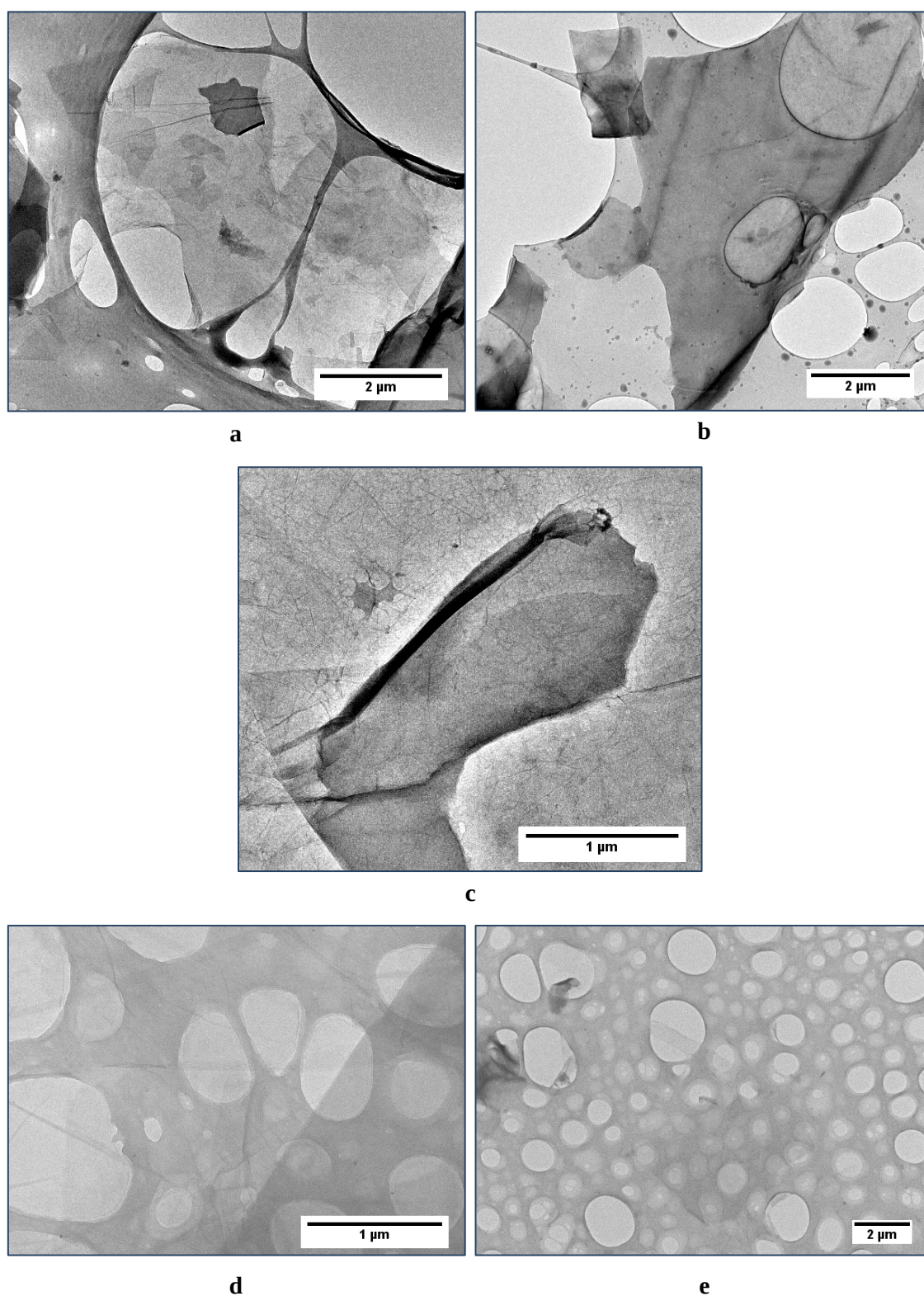


Figure 7-3 TEM images of the GO flakes produced from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively.

X-Ray Diffraction (XRD)

The XRD pattern for the natural flake graphite used is provided below in Figure 7-4. This pattern exhibits a single peak at $2\theta = 26.630^\circ$. This corresponds to a d -value of 3.35 Å. This is consistent with the expected result for the diffraction peak for graphite ($\approx 26^\circ$) [102, 111]. Following oxidation of the graphite, this diffraction peak decreases drastically in intensity [113]. The XRD patterns for the GO produced via the five experimental methods is presented in a combined plot, as shown in Figure 7-5. The diffraction peak for GO is located at $2\theta \approx 11^\circ$ [113], however, it has also been reported to lie at $2\theta \approx 10^\circ$ in the literature [107]. This means that the d -value varies between 8.04 Å and 8.84 Å. Therefore, the diffraction peak for GO may lie between these two points. The GO diffraction peak was found at the following positions for the different methods: 10.928° , 10.575° , 9.974° , 10.129° and 10.692° for Experiments 1- 5 respectively. This corresponds to the following d -values: 8.09 Å, 8.36 Å, 8.86 Å, 8.73 Å, and 8.27 Å for Experiments 1-5 respectively. All of these peaks are clear and defined and fall within the expected range for the diffraction peak of GO therefore the successful production of GO was confirmed.

An additional, far weaker peak was also present in the XRD pattern for GO, as seen in Figure 7-5. This peak was located at 26.637° , 26.487° , 23.817° and 24.999° for Experiments 1, 2, 4 and 5, respectively, while it was absent in the XRD pattern of the GO from Experiment 3. This peak is an indication of the residual graphitic material present in the sample which was not oxidised sufficiently since the graphite diffraction peak located at approximately $2\theta = 26^\circ$ [102, 111] gradually reduces in intensity as the graphite is oxidised [113]. The XRD pattern for the GO from Experiment 3 does not show any evidence of this peak therefore it can be deduced that this method resulted in the oxidation of most, if not all, of the graphite and therefore the best quality of GO. This peak was most intense in the GO from Experiment 1 and was of a lower intensity for the other three experiments. This indicated that the conversion efficiency from graphite to GO for this method was the lowest. The observed weak peaks present in the XRD sample of the GO from Experiment 4 between 15° and 25° were identified as residual potassium compounds. This implied that the purification method requires refinement in order to remove these residues.

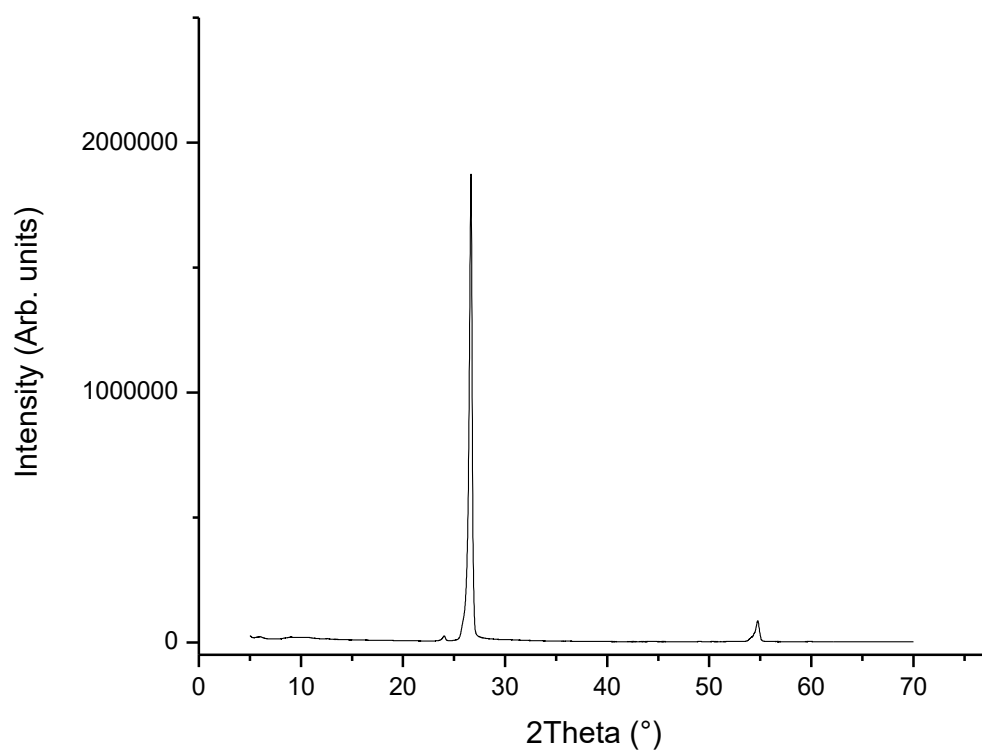


Figure 7-4 XRD pattern for graphite.

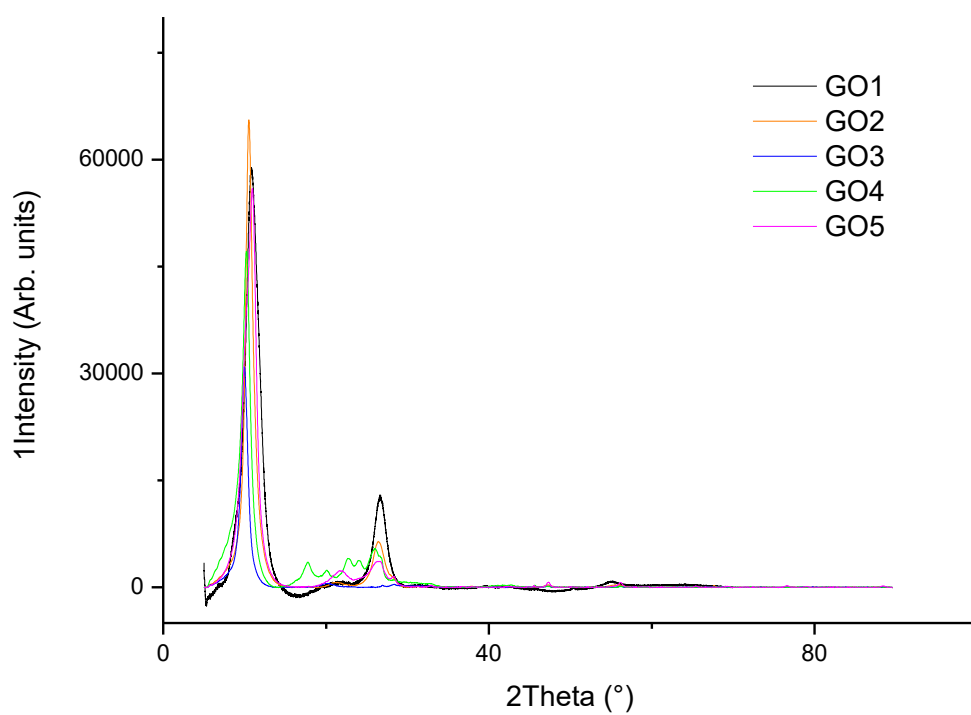


Figure 7-5 XRD patterns of the GO produced from each of the five experimental methods.

Discussion of methods

Following the analysis of the microscopy and XRD data and also taking the qualitative analysis of the GO experiments (Section 5.5) into consideration, it was determined that Experiments 3 and 4 produced GO of the highest quality. Thus, since these products were deemed the highest quality, EDX was performed on the GO samples from these two methods to compare their relative degree of oxidation. The oxygen content as per the EDX analysis of Experiment 3 and 4 was: 37 wt. % and 38 wt. %, respectively. The EDX spectra for these samples may be seen in Figure 7-6 and Figure 7-7. This implied that the level of oxidation of the GO produced from these two samples was comparable. However, the carbon content as per the EDX analysis of Experiment 3 and 4 was: 59 wt. % and 56 wt. %, respectively. This implied that a greater amount of impurities was present in the GO sample from Experiment 4 than that of Experiment 3. This is also evident in the high sulphur (S) and chlorine (Cl) peaks which can clearly be seen in Figure 7-7. The Cl may be due to the HCl being insufficiently removed during the washing process. The large S peak was possibly a result of the H_2SO_4 being insufficiently removed during the washing process as well. Most of these impurities are in the form of residual material from the reagents used in the experiments which was not completely washed out of the sample during the purification process.

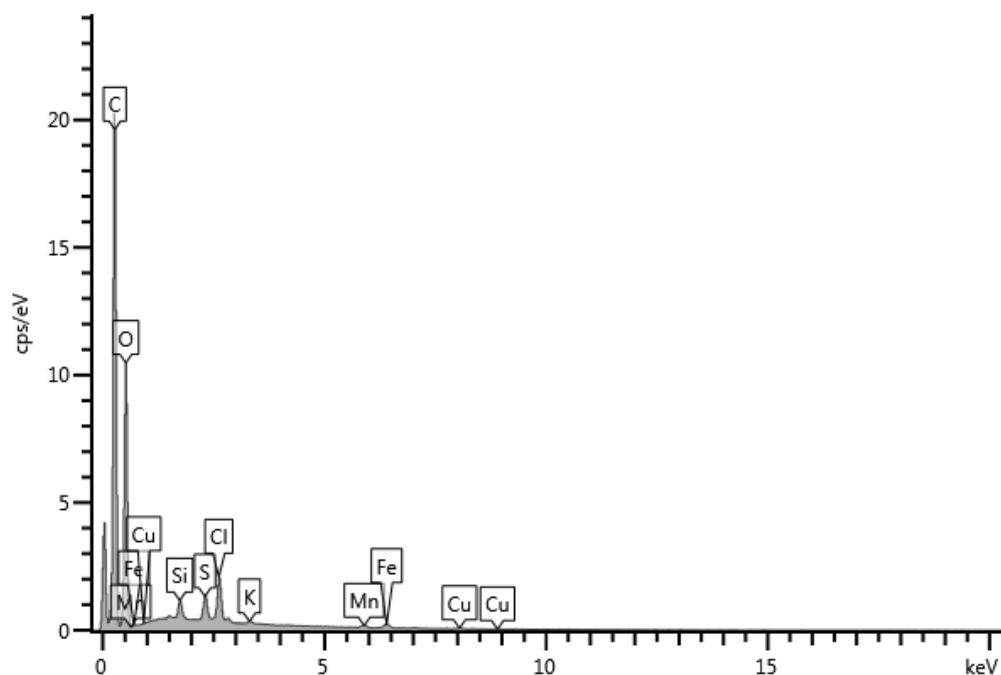


Figure 7-6 EDX spectrum from SEM for GO from Experiment 3.

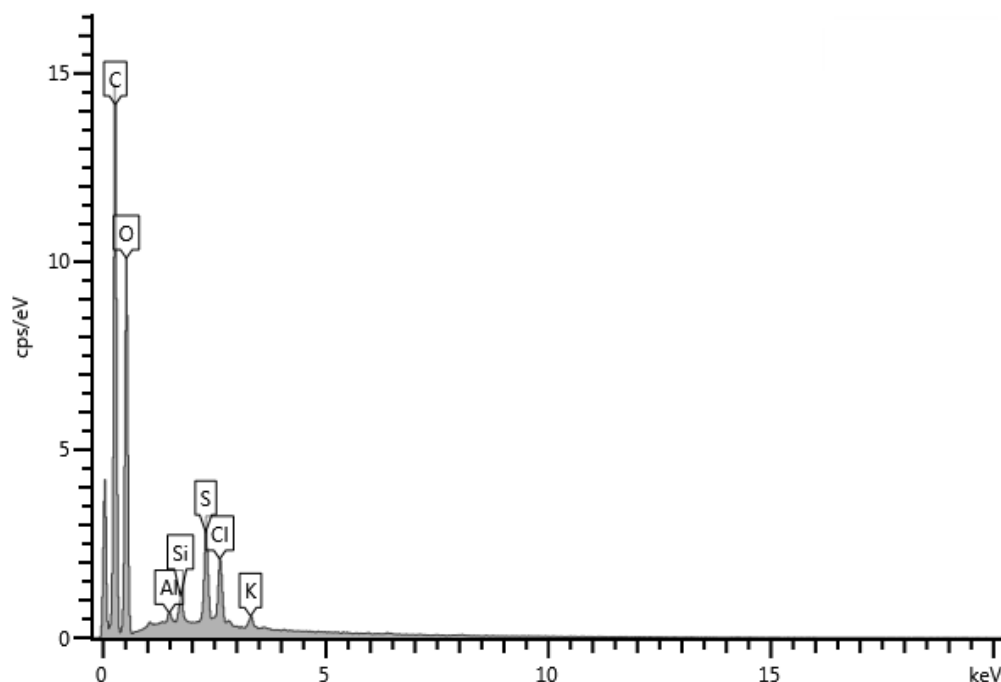


Figure 7-7 EDX spectrum from SEM for GO from Experiment 4.

7.2.2. Reduction of graphene oxide to form graphene

Sodium borohydride method

The SEM images of the graphene produced from the reduction of GO via NaBH_4 from the various experiments did not provide significant information about the graphene. The common observation from these images was that the flake size had reduced somewhat following reduction of the GO. All five experiments produced graphene flakes with wrinkled surfaces that were mostly likely caused by the reduction mechanisms and/or impurities [74]. It should be noted, however, that the graphene produced from Experiment 5 appeared very similar to graphite. These images may be seen in Figure 7-8. The TEM images provided more valuable information with regards to the structure of the synthesised graphene. Images a and b of Figure 7-9 are quite similar in that graphene flakes were observed that were highly electron transparent which indicated that the material consists of only a few layers of graphene. The surface of these flakes was smooth as well, although some folding was observed. Image c also depicts a highly electron transparent graphene flake with areas of highly crinkled folds in the flake. This high magnification image may be seen in Figure 7-10. The general surface of this graphene flake was far rougher and more wrinkled than the other flakes. Images d and e are largely similar as both the observed graphene flakes were highly electron transparent. The only difference was that the graphene from Experiment 5 was larger and slightly darker which suggests that it was composed of more graphene layers than the other graphene flakes. The flakes from images d and e of Figure 7-9 were smoother than that of Experiment 3 but rougher than that of Experiments 1 and 2. Although, it should be noted that the images d and e were taken using the TEM that was operated at 100 kV rather than the TEM

operated at 200 kV as the microscope was inoperable at the time. Therefore, the sheets may appear slightly less transparent.

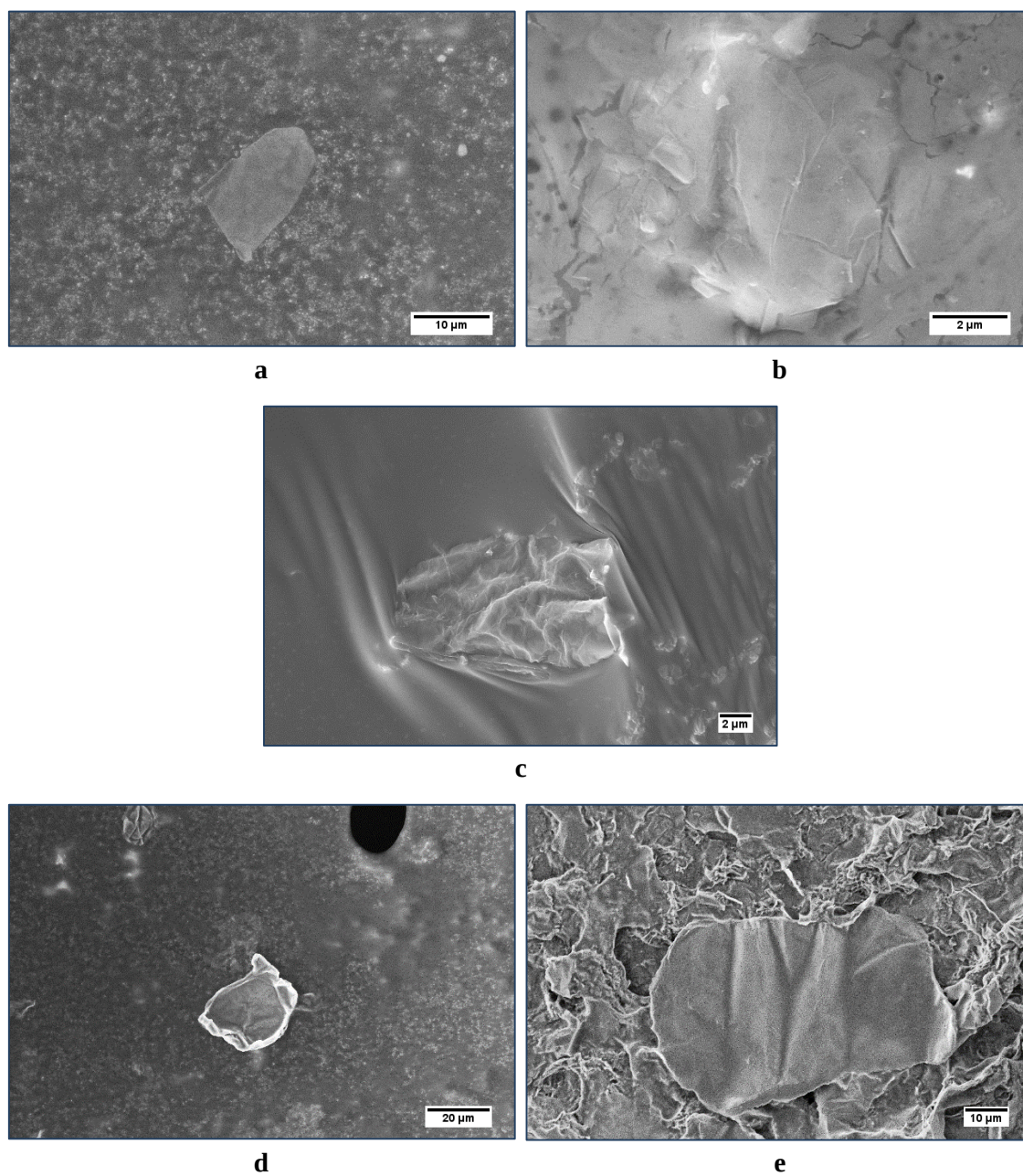


Figure 7-8 SEM images of GO reduced via NaBH_4 . Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO_4 , the Tour method, and the Huang method, respectively.

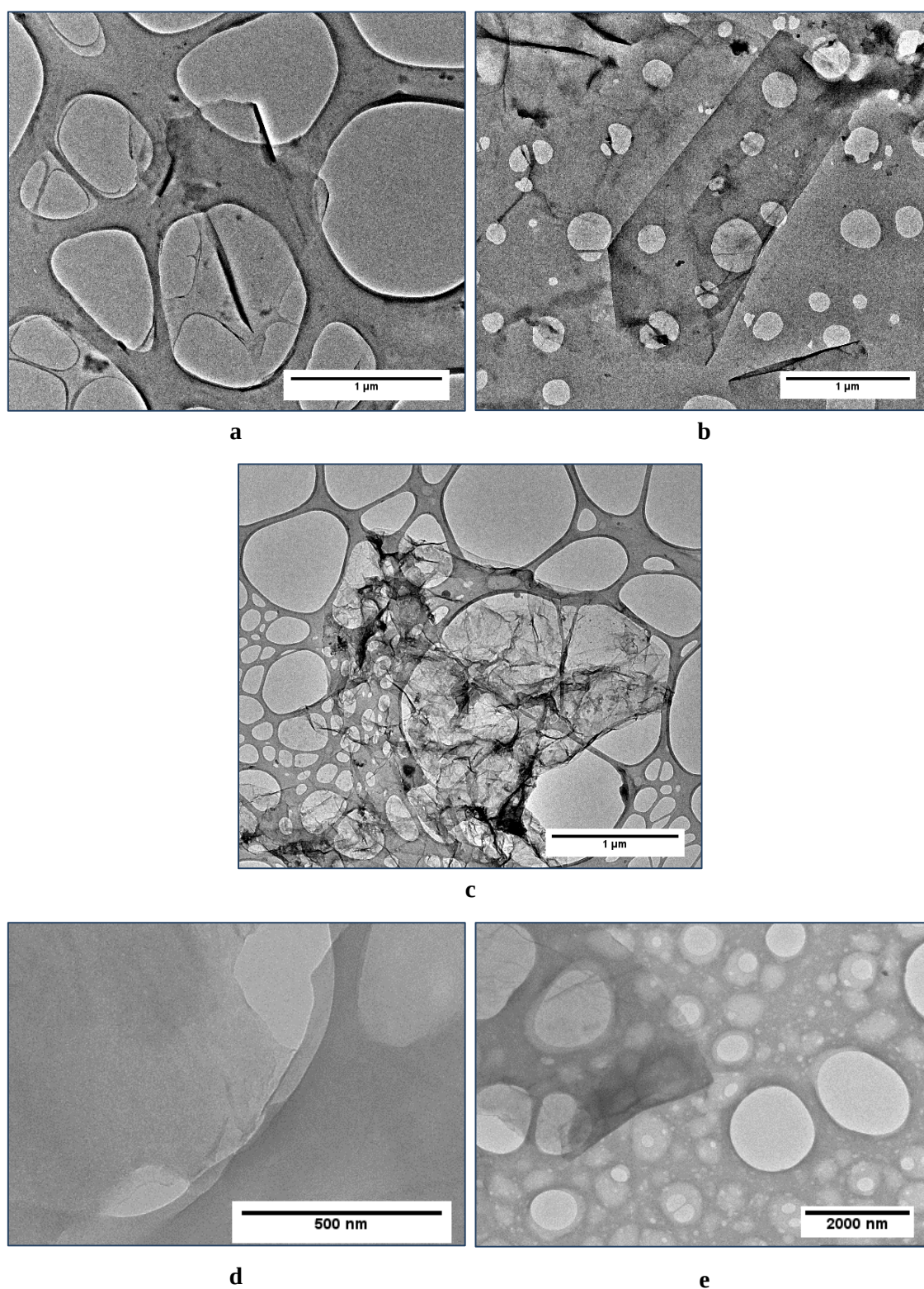


Figure 7-9 TEM images of the graphene produced using the NaBH₄ method from each of the five experiments. Images a - e indicate the Hummers' method, the modified Hummers' method with extended oxidation time, the modified Hummers' method with additional KMnO₄, the Tour method, and the Huang method, respectively.

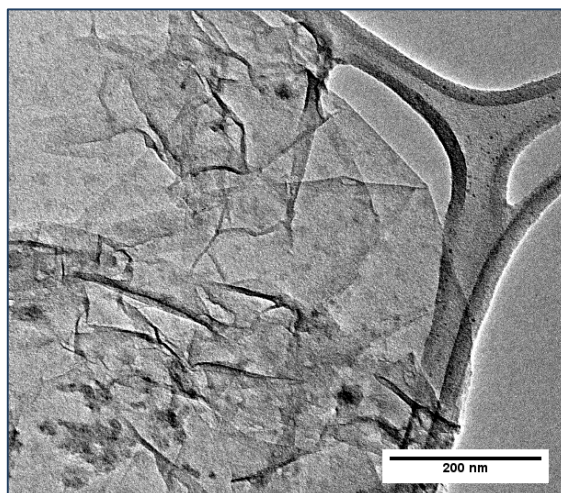


Figure 7-10 TEM image of graphene from Experiment 3 produced using the NaBH₄ method.

The XRD patterns for the graphene produced from Experiments 3 and 4 using the NaBH₄ reduction method are presented in Figure 7-11. Only the graphene samples synthesised from the GO of these two experiments were analysed using XRD since these methods were determined to produce the highest quality of GO. Thus graphene of a similar, high quality was expected from the reduction of these samples. The plot has been scaled down for comparison purposes with the XRD patterns of the other reduction methods. The expected graphene diffraction peak is located between $2\theta \approx 24^\circ - 26^\circ$ [112], the corresponding d -value range is $3.42 \text{ \AA} - 3.70 \text{ \AA}$. The intensity of this peak is an indication of the number of graphene layers present with the intensity increasing proportionally with the number of graphene layers [112]. For few-layer graphene, a low intensity broad peak is expected [112]. The XRD pattern for the graphene from Experiment 3 did not exhibit a definite single peak but formed a few peaks of similar intensities. This suggests that the reduction of the GO from this experiment resulted in the production of graphene with various lattice plane distances. As the peaks are quite broad, this may indicate few-layer or single layer graphene. However, the two prominent peaks correspond to d -values of $5.16 \text{ \AA}$ and $3.06 \text{ \AA}$. The XRD pattern for graphene from Experiment 4 resembled the expected results for graphene more closely since a broad, low-intensity peak was formed. When the data from both plots were further processed by using a smoothing, multi-peak function to form a single, broad, low-intensity peak, the peak centre was located at $2\theta = 22.359^\circ$ and $2\theta = 24.606^\circ$ for the graphene produced from Experiment 3 and 4, respectively. This corresponds to d -values of $3.97 \text{ \AA}$ and $3.62 \text{ \AA}$, respectively. These XRD patterns can be seen in Figure 7-16. Thus, this data implied that the resulting reduced material resembled graphene quite closely, however the reduction process must be refined in order to ensure a higher quality and uniformity of graphene. Although, the diffraction peak for graphene from Experiment 4 did lie within the expected range thus this material resembled the expected results more closely. The smoothed, multi-peak fitted data (Figure 7-16) has been included in this

section, however, the unprocessed data (Figure 7-11 and Figure 7-15) has also been included so that misrepresentation of the results did not occur.

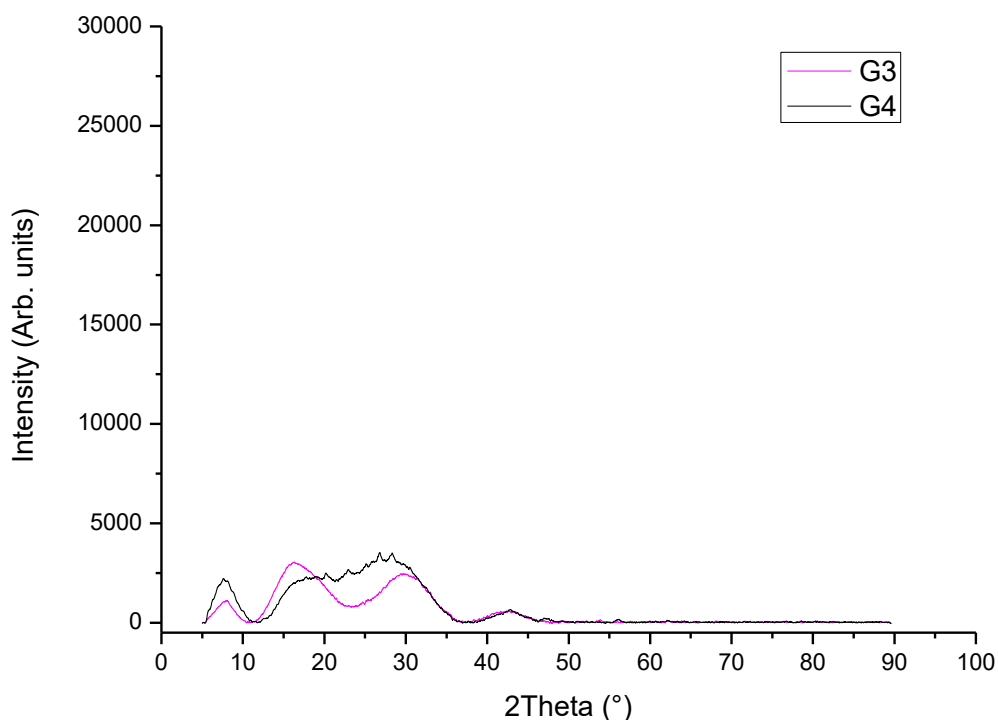


Figure 7-11 XRD patterns of graphene produced from Experiments 3 and 4 via the NaBH_4 reduction method. G3 indicates the XRD pattern of graphene from Experiment 3, and G4 indicates the XRD pattern of graphene from Experiment 4.

As mentioned previously, it was determined that Experiments 3 and 4 produced GO of the highest quality. Thus EDX was performed on the graphene samples resulting from the reduction via NaBH_4 of the GO from these two methods to compare their relative degree of reduction. These spectra are depicted below in Figure 7-12 and Figure 7-13. The oxygen content as per the EDX analysis of Experiment 3 and 4 was: 19 wt. % and 30 wt. % respectively. This implied that the graphene synthesised via Experiment 3 was reduced to a greater extent than that from Experiment 4 as the oxygen content for the GO from Experiment 3 was reduced by 18 wt. % while this figure was only 8 % for the GO from Experiment 4. This served to confirm the observation that was made during the filtration of the graphene from Experiment 4 since the solution remained slightly brown an hour after the addition of the NaBH_4 . The presence of the brown colour indicated that GO was still present as a complete reduction of the sample would have resulted in a black coloured solution [230]. Another implication of the varying oxygen composition of the two graphene samples was that NaBH_4 may not be the ideal reducing agent for the GO produced from Experiment 4. The properties of this GO varied from that of the GO produced from Experiment 3 since the oxidising agents were different therefore the oxidation mechanism would have been different. Also, the resulting GO may not have been as efficiently reduced using the same reducing agent. Furthermore, there was a high sodium content present in the graphene samples from

Experiment 4. This indicated that the NaBH_4 was not sufficiently washed out of the sample. To correct this, the samples should be washed multiple times with ethanol and filtered.

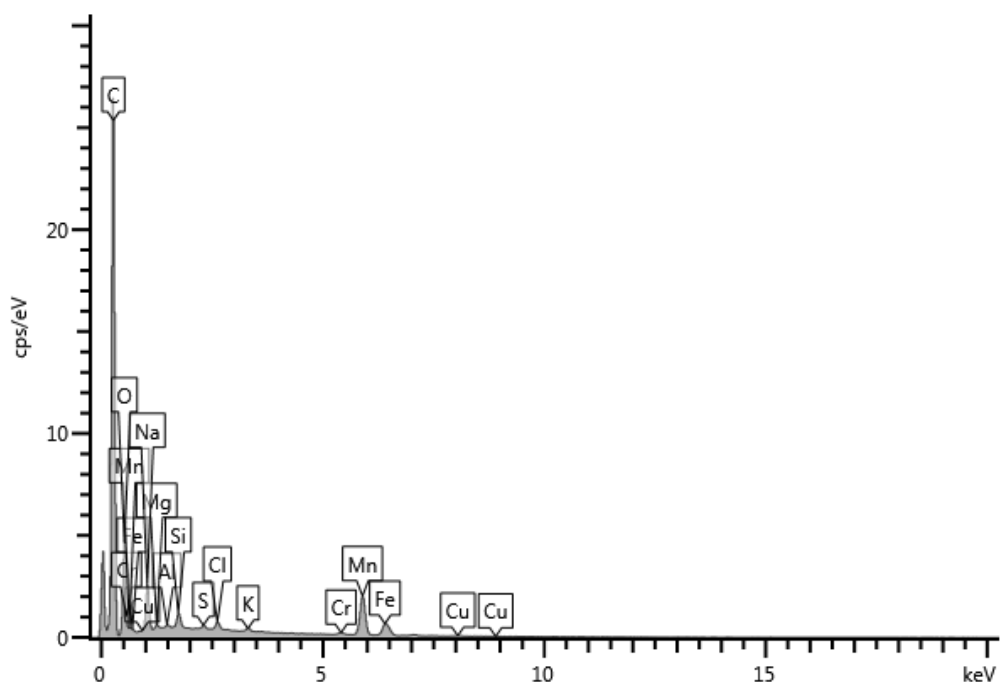


Figure 7-12 EDX spectrum from SEM of graphene produced from Experiment 3 via the NaBH_4 reduction method.

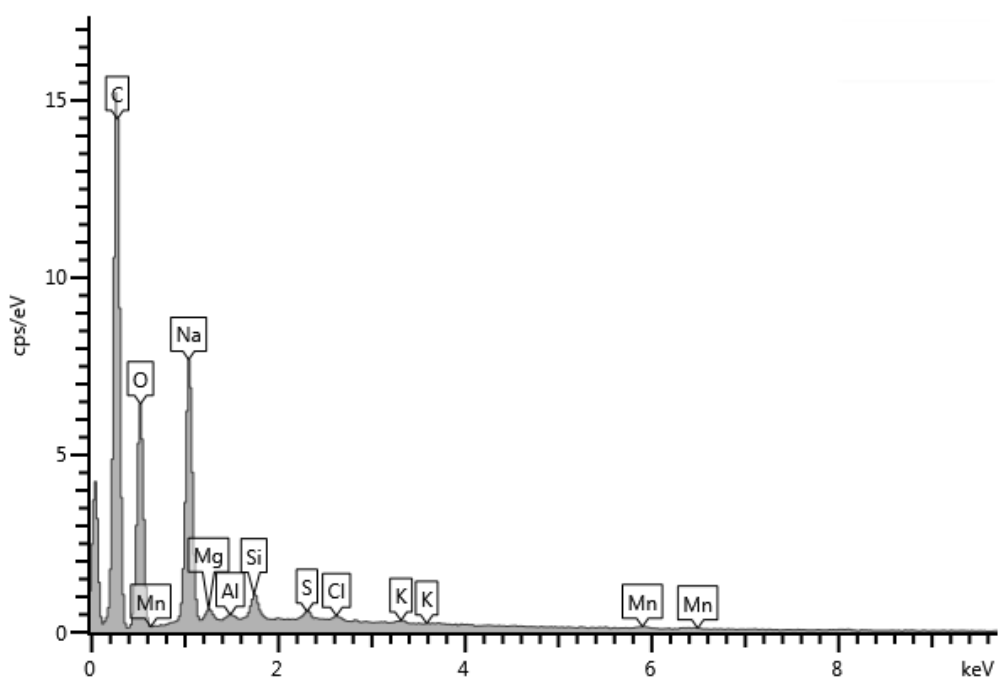


Figure 7-13 EDX spectrum from of graphene produced from Experiment 4 via the NaBH_4 reduction method.

The results from the microscopy, XRD and EDX data suggest that this method of reduction produced graphene of a fairly high quality since the TEM images revealed mostly smooth, transparent flakes, and EDX analysis indicated that 8 – 18 wt. % of the oxygen was removed. This suggested that the resulting graphene still contained a small degree of oxygen-functionalisation. The reason for the shortfalls of this method as reported by Yang *et al.* [74] could

be that NaBH_4 was able to reduce $\text{C}=\text{O}$ groups efficiently, carboxylic acids to a lesser extent and poorly reduced hydroxyl groups. The presence of these groups as well as the defects introduced through the oxygen reduction could be responsible for the discrepancy between the experimental results and the expected results from the literature [74]. These functional groups may be more efficiently removed through the use of a CaCl_2 catalyst [74] as well as by increasing the amount of NaBH_4 used for the same concentration of GO.

Ascorbic acid method

The TEM images below of the graphene produced from the GO of Experiment 4 via the ascorbic acid (AA) reduction method revealed quite small graphene flakes. The surface of these flakes appeared rough and wrinkled which was most likely an effect of the extended ultrasonication period of 6 hours. The flakes are also not as electron transparent as those observed from the NaBH_4 method above which suggested that this graphene consisted of a greater number of layers.

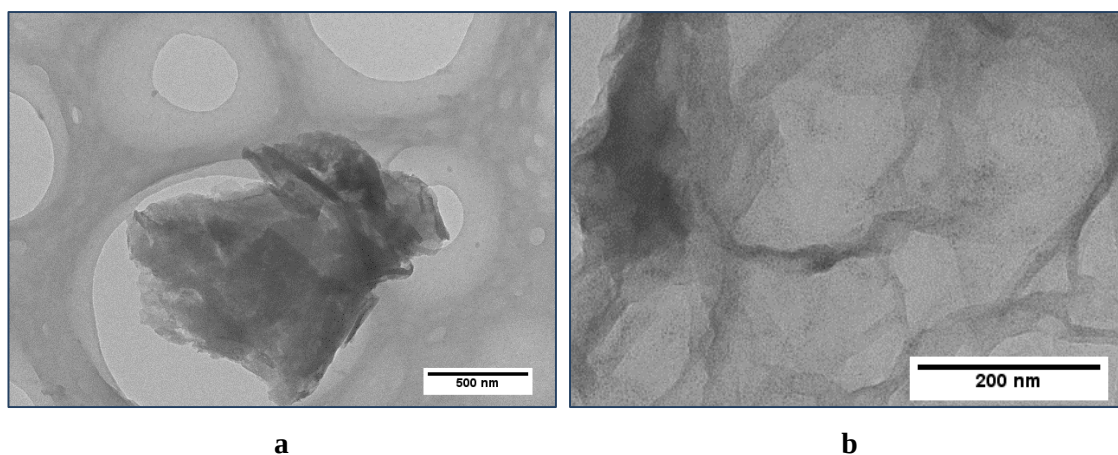


Figure 7-14 TEM images of the graphene synthesised from GO via the ascorbic acid method at low magnification (a) and high magnification (b).

The XRD pattern for the graphene produced from Experiment 4 using this reduction method is presented in Figure 7-15. This XRD pattern also does not exhibit a definite single peak but forms a cluster of peaks of similar intensities. When this data was further processed by using a smoothing, multi-peak function to form a single, broad, low-intensity peak, the peak was located at $2\theta = 22.770^\circ$. The corresponding d -value of this peak is $3.90 \text{ \AA}$. This XRD pattern can be seen in Figure 7-16. These data implied that the resulting reduced material resembled graphene fairly closely, however, the reduction process must also be optimised to ensure that the resulting product resembles pristine graphene more closely in morphology and structure.

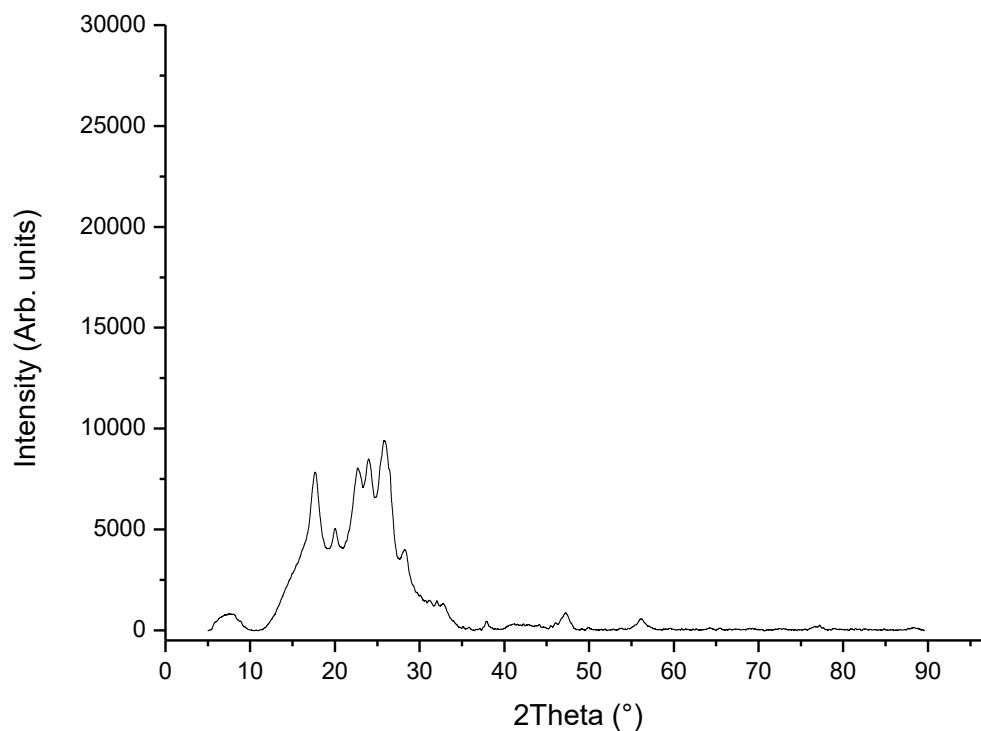


Figure 7-15 XRD pattern of graphene produced from Experiment 4 via the ascorbic acid reduction method.

The microscopy data, as seen in Figure 7-14 above, showed that the material consisted of small flakes with rough surfaces, multiple layers and topological defects which were not nearly as prevalent using the other reduction methods. This consequence was inherent to this process due to the ultrasonication required to aid the reduction reaction [233]. However, the advantage of this method was the nontoxic, environmentally friendly nature of this reducing agent since harsher chemical reducing agents are unwanted in graphene-related applications [233].

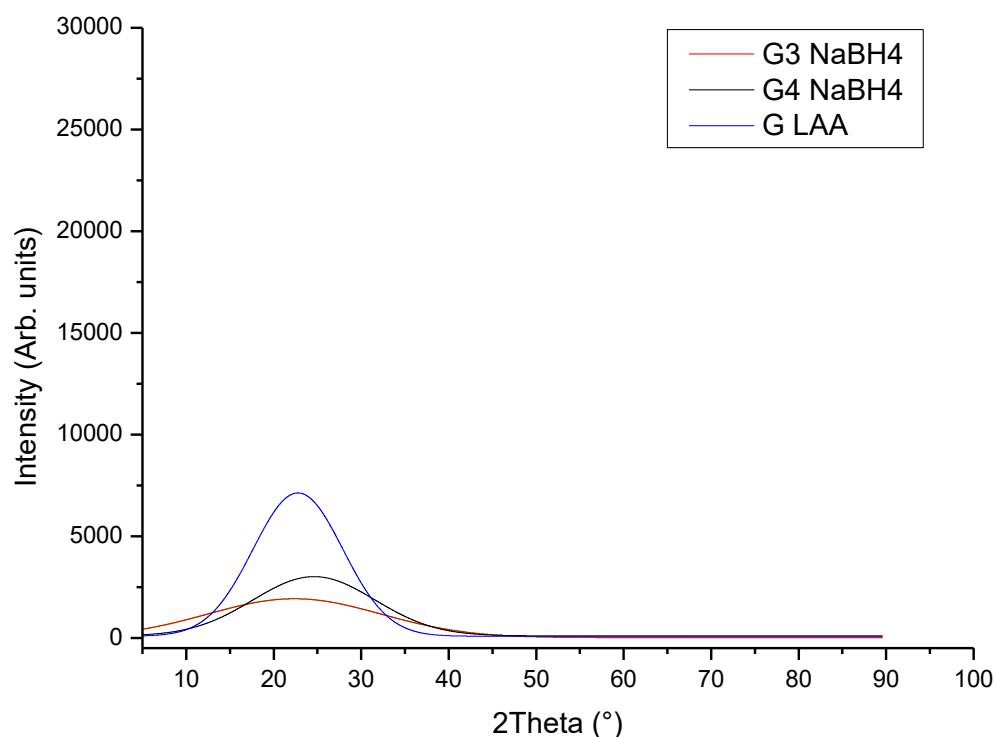


Figure 7-16 Multi-peak fitted XRD patterns for the graphene resulting from the chemical reduction of GO. G3 NaBH₄ and G4 NaBH₄ indicates the XRD pattern of the graphene produced from the GO from Experiment 3 and 4 respectively through the use of NaBH₄. G AA indicates the XRD pattern of the graphene produced from the GO from Experiment 4 which was reduced via ascorbic acid.

Thermal treatment method

The TEM images of the graphene produced from the GO of Experiment 3 via the thermal treatment reduction method revealed large graphene flakes that were highly electron transparent. However, impurities were present on the flakes as well, as seen in Figure 7-17. These images were taken from the first experiment of this section where the GO was exposed to 1000 °C for 1 hour. The EDX analysis also revealed the presence of foreign material, as discussed below. This contamination present may have been introduced by the TEM. However, EDX analysis of the second experiment of this section where the GO was exposed to 1000 °C for 3 hours indicated that most of these contaminants had been removed. The EDX data is discussed later in this section.

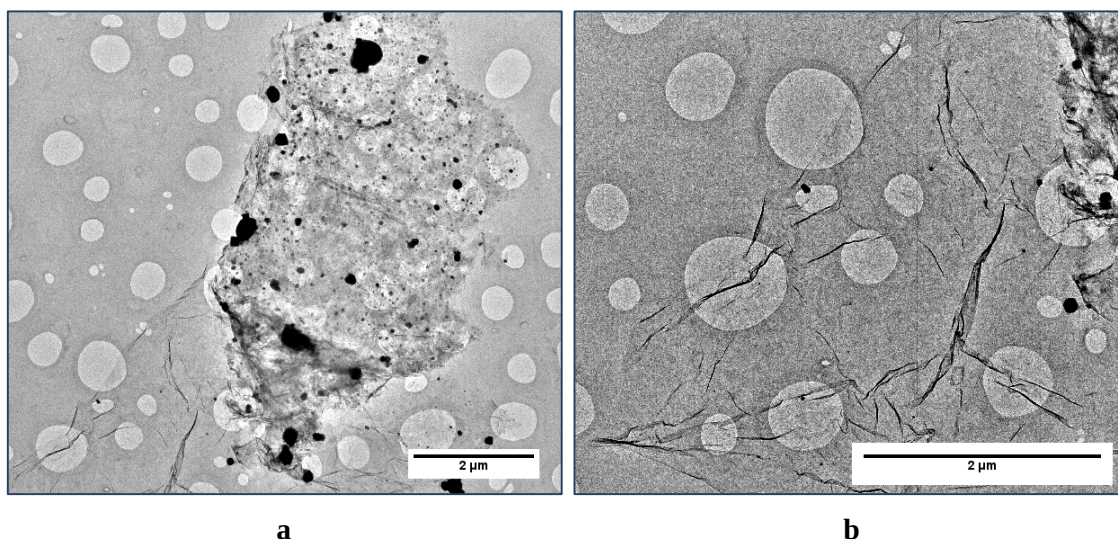


Figure 7-17 TEM images of the graphene synthesised from GO via the thermal treatment reduction method at low magnification (a) and high magnification (b).

The XRD pattern for the graphene produced from Experiment 3 using this reduction method is presented in Figure 7-18. This XRD pattern exhibits a definite single peak located at $2\theta = 26.776^\circ$. The corresponding d -value for this peak is $3.33 \text{ \AA}$. This result lies within the expected range for the graphene diffraction peak from literature ($3.35 \text{ \AA}$) [112]. Thus, this data implies that graphene was synthesised [112]. This may have been caused by the partial annealing which the material experienced while left to cool naturally to room temperature. This XRD pattern does not exhibit the broad peak as seen in the XRD patterns of Figure 7-11, Figure 7-15 and Figure 7-16. This suggests that the graphene consisted of several layers of graphene. However, when compared to the XRD pattern for graphite in Figure 7-4, it can be seen that the intensity of the diffraction peak of this graphene is orders of magnitude below that of graphite, therefore it is not graphitic.

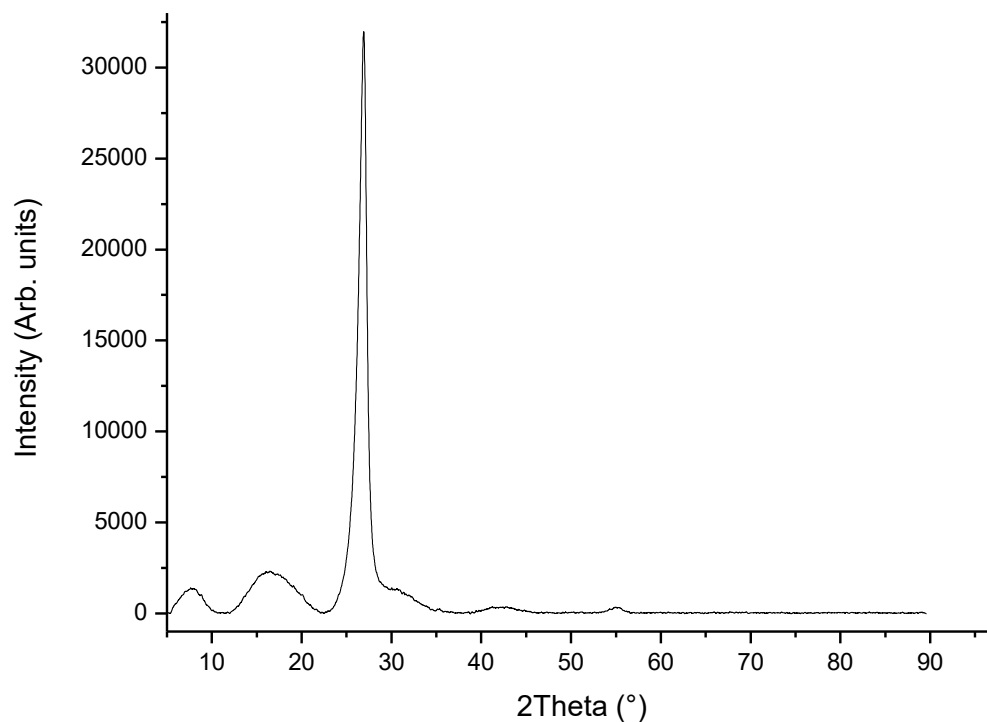


Figure 7-18 XRD pattern of graphene produced from Experiment 3 via the thermal treatment reduction method.

As already mentioned, the graphene from the first experiment using this method appeared to have a high degree of contamination present. This can be seen in the spectrum of Figure 7-19 below. However, this was removed from the sample during the second experiment, as seen from the EDX spectrum below. The increased exposure time to the high temperature could be responsible for the removal of these contaminants from the graphene. The oxygen content of the GO from Experiment 3 was 37.10 wt. % and after reduction via exposure to elevated temperatures for 1 hour, this was reduced to 10.96 wt. %. This figure was further improved upon when the experiment was repeated, and the exposure time was increased to 3 hours to achieve graphene with an oxygen composition of only 9.68 wt. % which is the lowest oxygen content of all the synthesised graphene. The low-intensity peaks for iron (Fe), chromium (Cr), manganese (Mn) and molybdenum (Mo) may be present due to the microscope itself or from the holder, rather than from the sample.

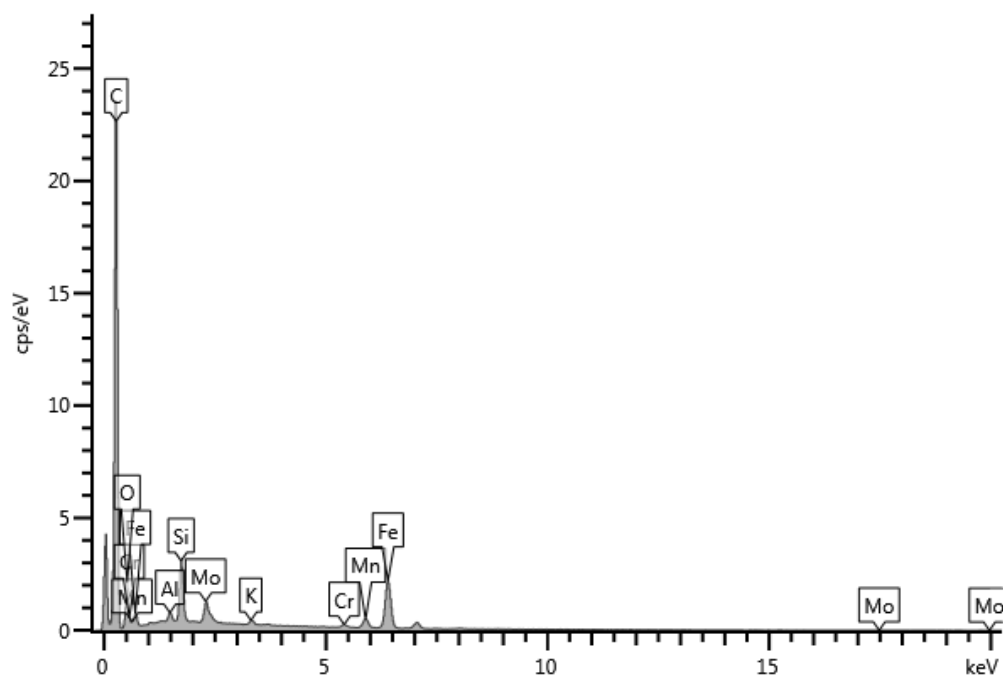


Figure 7-19 EDX spectrum from SEM of the graphene synthesised via the reduction of the GO from Experiment 3 using the thermal treatment reduction method with an exposure time of 1 hour.

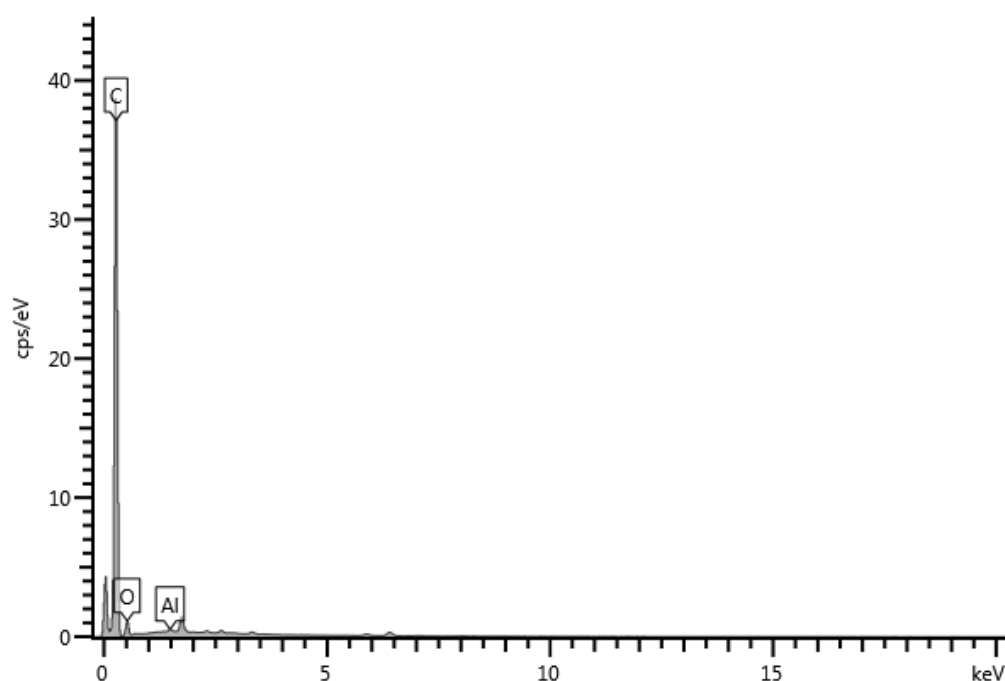


Figure 7-20 EDX spectrum from SEM of the graphene synthesised via the reduction of the GO from Experiment 3 using the thermal treatment reduction method with an exposure time of 3 hours.

7.2.3. Discussion of methods

The GO produced was of a high quality, as indicated by the microscopy images as well as XRD data. The XRD data confirms the qualitative analysis of the produced GO since the XRD data of the GO from the Tour method conforms most closely with the results from literature and

is therefore the most oxidized product. The GO produced from all five samples showed clear correlation with that of the expected results from the literature, however, the results from the reduction of this GO are not of the same standard. The exemption to this is the thermal reduction route. This indicates that the method of reduction needs to be improved upon to produce graphene which resembles previous results more closely.

The reduction method of the thermal treatment of GO resulted in graphene of a highly ordered nature, however, this reduction route introduces significant topological defects in the resulting material thus potentially adversely affecting its electronic properties [65]. However, from literature, the reported conductivity of the produced graphene remains fairly high following thermal reduction which indicates that this method of reduction is satisfactory [70].

The characterisation of the GO and graphene produced could be improved by obtaining the electron diffraction pattern for the samples. This would aid in the determination of the number of layers within the graphene samples in particular.

It is clear that the method of reduction needs to be optimised for the specific application of interest. The most desirable properties of graphene include its large surface area and high conductivity, therefore, the optimised reduction route should produce graphene possessing these qualities.

The produced graphene and graphene oxide may be used in a number of applications which include transistors, photovoltaic cells [45] and strengthening fillers [6, 240].

7.3. Results of the electrospinning of graphene fibres

The SEM images of the fibres produced from the individual experiments have been presented in Chapter 6 while this section serves to present the influence of the various parameters on the fibre morphology. It has already been deduced that the experiment which produced the desired fibre composition and morphology was Experiment III detailed in Section 6.9 with the following parameters: needle gauge of 18 G, flow rate of 70 $\mu\text{l}/\text{min}$, applied voltage of 20 kV, tip-to-collector distance of 15 cm, PVA solution concentration of 12 % (wt. /vol.), and graphene concentration of 5 % (wt. /vol.). This experiment resulted in the optimal graphene nanofibre production, as determined by the extensive electrospinning experiments that were conducted.

Tip-to-collector distance

When only PVA solutions were electrospun, it was observed that the size and prevalence of the beading present on the fibres decreased with increasing tip-to-collector distance. And a converse decrease in this distance served to increase the area of deposition of the fibres. Evidence of both of these observations can be seen in Figure 7-21. The beads were reduced from $\sim 4.63 \mu\text{m}$ to 784.86 nm. The same observed effect was noticed when PVA was electrospun with graphene

as an increase in the tip-to-collector distance resulted in more fine, less beaded fibres; this can be seen in Figure 7-22.

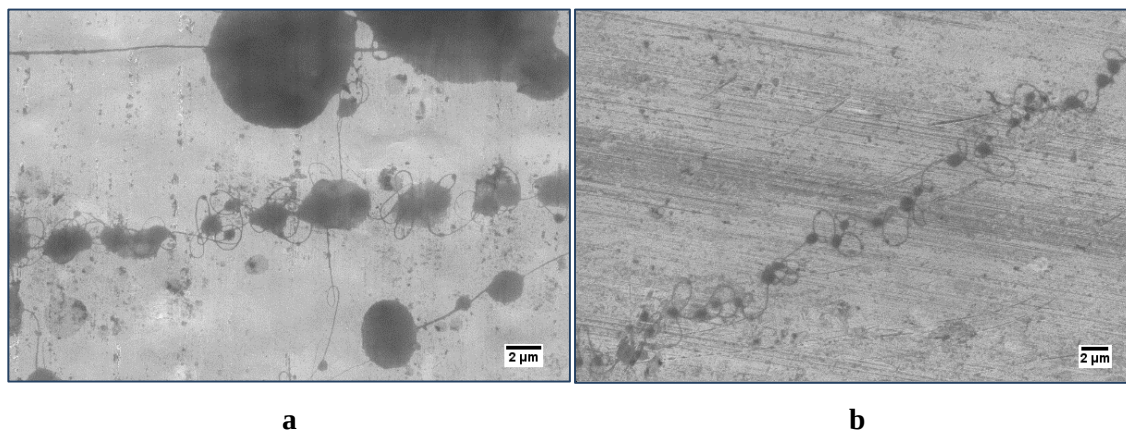


Figure 7-21 SEM images of PVA fibres produced from the electrospinning of 6 % (wt. /vol.) PVA solution at 3 cm (a) and 15 cm (b).

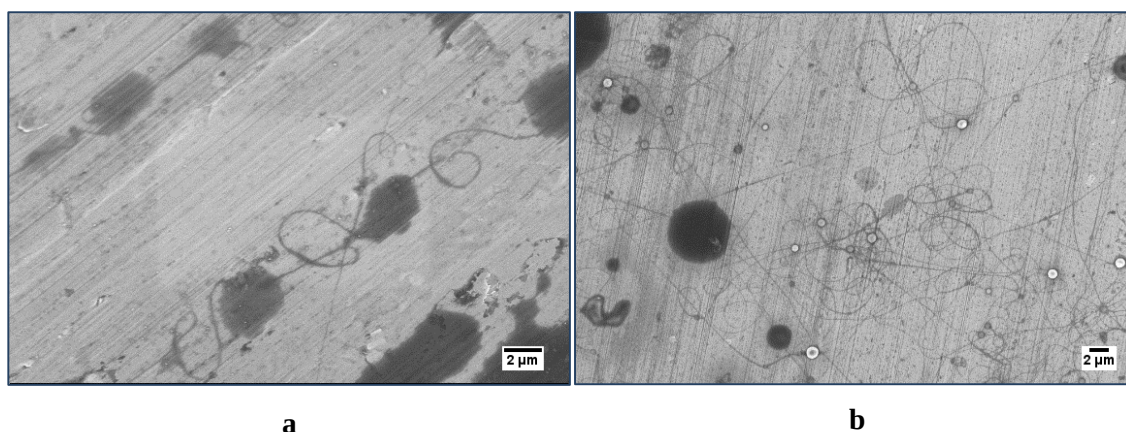


Figure 7-22 SEM images of PVA/graphene fibres produced from the electrospinning of 12 % (wt. /vol.) PVA solution with graphene at 5 cm (a) and 15 cm (b).

Flow rate

A significant decrease in flow rate below the critical point resulted in minimal fibre formation. However, for low flow rates which lay above the critical point, the fibres were deposited over a larger area however this could also be caused by droplets falling onto the collector if the apparatus was assembled in the vertical configuration. Figure 7-23 depicts the presence of multiple fibres at a flow rate of 180 µl/min while at a rate of 90 µl/min, for the same solution and with the other processing parameters held constant, there was minimal fibre production.

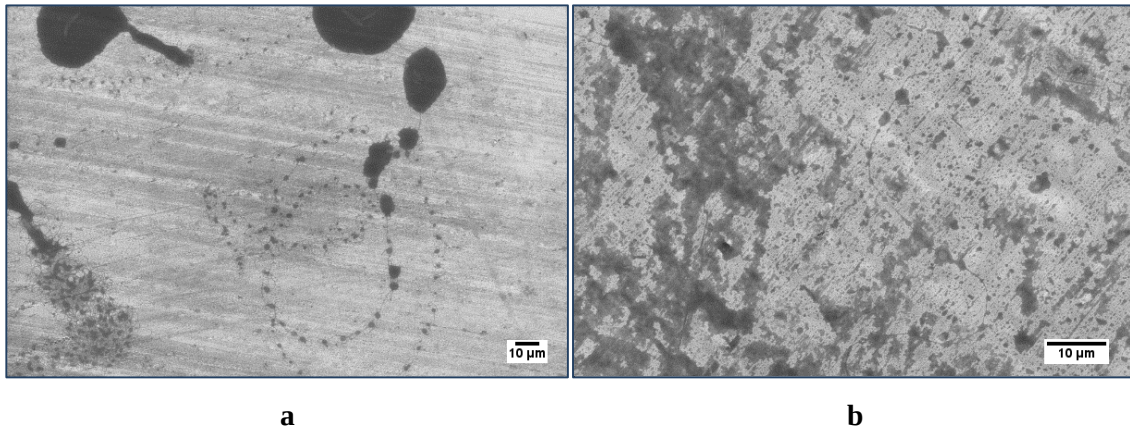


Figure 7-23 SEM images of PVA fibres produced from the electrospinning of 6 % (wt. /vol.) PVA solution at 180 µl/min (a) and 90 µl/min (b).

Applied voltage

An increase in the applied voltage appeared to result in a sparser distribution of the fibres, as seen in the figure below. This is observed because a higher applied voltage results in an electrospinning jet which is more unstable therefore the whipping motion of the jet is greater which leads to a sparse deposition of the fibres. These fibres also have less beading present and appear more uniform.

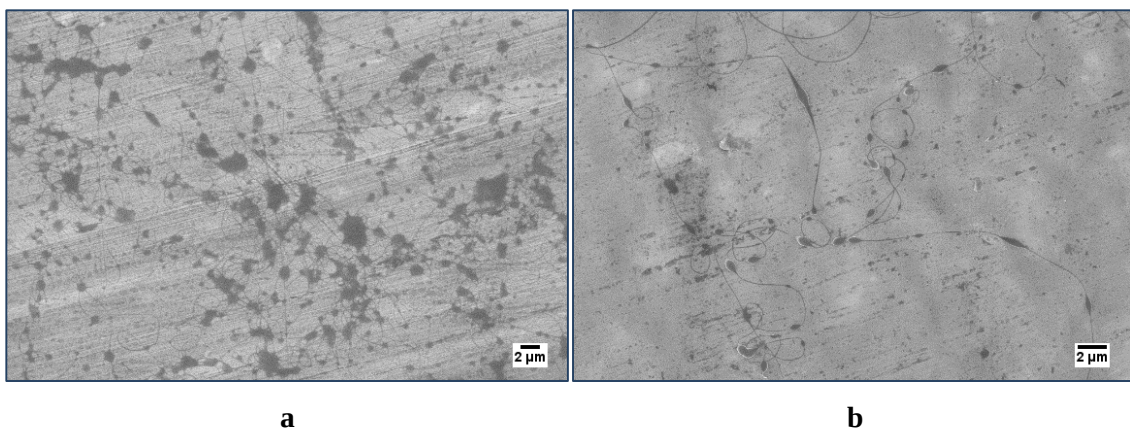


Figure 7-24 SEM images of PVA fibres produced from the electrospinning of 4 % (wt. /vol.) PVA solution at 20 kV (a) and 22 kV (b).

Solution concentration

When pure PVA solutions were electrospun, it was noted that the electrospinning of solutions of higher concentrations resulted in a higher quality of fibres. The prevalence and size of the beads on the fibres appeared to be reduced with an increase in the solution concentration. Also, the diameter of the electrospun fibres increased with an increase in solution concentration however the diameters then appeared to decrease once more. This could be caused by the flow rate instead which may have been too high when using the 10 % (wt. /vol.) PVA solution which resulted in the web-like appearance of the fibres. This flow rate remained constant for the

12 % (wt. /vol.) PVA solution however the viscosity of this solution is higher thus the effect of the high flow rate would be mitigated because of this. Hence, resulting in the production of finer fibres.

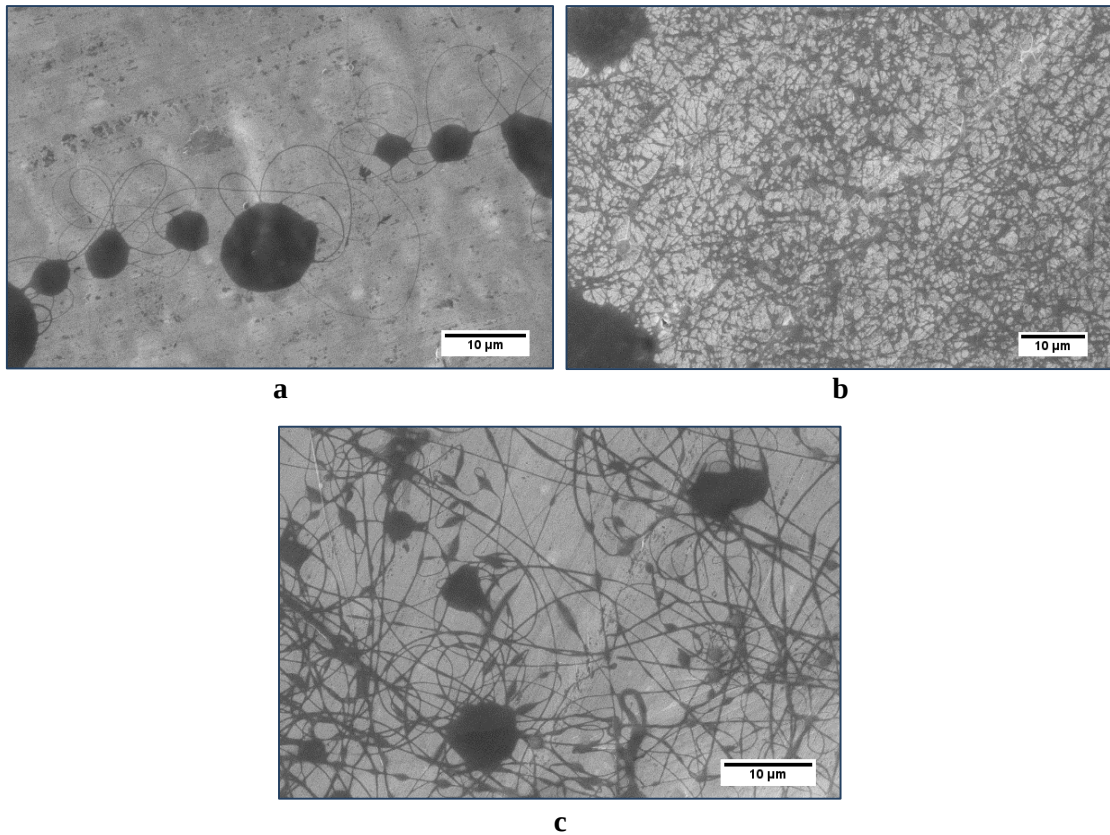


Figure 7-25 SEM images of PVA fibres produced from the electrospinning of 4 % (wt. /vol.) (a), 10 % (wt. /vol.) (b) and 12 % (wt. /vol.) (c) PVA solutions.

Optimal electrospinning experiment results

The experiment which resulted in the fabrication of fibres possessing the desired composition and morphology was Experiment III detailed in Section 6.9 with the following parameters: needle gauge of 18 G; flow rate of 70 µl/min; applied voltage of 20 kV; tip-to-collector distance of 15 cm; PVA solution concentration of 12 % (wt. /vol.); and graphene concentration of 5 % (wt. /vol.). Images of the fibres produced using these parameters can be seen in Figure 7-26. A network of fine fibres was produced with little or no beading present on the fibres. The average diameter of these electrospun fibres was 107.40 nm.

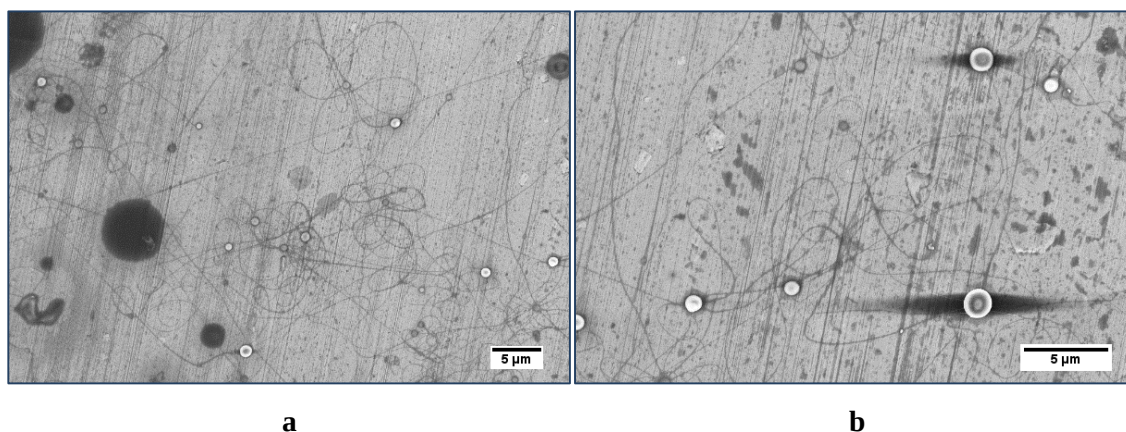


Figure 7-26 SEM images of PVA/graphene fibres produced via the electrospinning of 12 % (wt. /vol) PVA solution with graphene using the determined optimal parameters observed at low magnification (a) and high magnification of the same area (b).

7.4. Summary

The analysis of the synthesised GO and graphene confirmed that these products were consistent with that from literature. The synthesised GO, in particular, was of a high standard. Although the results from the reduction of this GO leave room for improvement. While it was confirmed that graphene was in fact produced, it was found that the quality of this material may be improved upon to produce graphene which resembles theoretical findings more closely. However, graphene in this form may still find applications in the form of supercapacitors for example.

The electrospinning experiments were not the main focus of this research, hence a brief investigation into the dimension and morphology of spun graphene composite fibres was conducted. The size and morphology of the fibres produced from the investigated fibre fabrication method may be optimised for specific applications. The possible applications of these produced fibres lies primarily in the field of composite materials where the fibres may act as strengthening components. There is also scope for the conducting properties of these fibres to be improved upon and tuned for electrical-related applications. This research successfully showed how graphene could be drawn into fibres.

Chapter 8 Conclusions

The results of this dissertation established foundational graphene-related research which entailed the production of graphene through chemical oxidation of graphite and reduction via thermal and chemical routes. The products were analysed using electron microscopy, EDX and XRD techniques. These diagnostic tools enabled the products to be analysed to determine the quality thereof and hence to deduce the efficiency of each of the five explored experimental methods. Another outcome of this research was the fabrication of graphene fibres. The morphology of the fibres was investigated through the use of electron microscopy imaging techniques. SEM analysis confirmed that graphene nanoscale fibres were produced.

The chemical synthesis as presented in this dissertation provided a potentially low-cost method through which to synthesise GO in fairly large quantities as this method is scalable. Graphene has successfully been synthesised using the Hummers' method, various modified versions of the Hummers' method, the Tour method and a modified version of this method. The GO resulting from each of these methods was compared based on the degree of oxidation of each sample. The graphene produced was similarly analysed by comparing the degree of reduction (or deoxygenation) of the samples. It was deduced that the most efficient methods for the production of high quality GO was the modified Hummers' method (Experiment 3) and the Tour method (Experiment 4). Both these experimental methods proved most suitable for execution in the laboratory. The XRD and microscopy data collected from the various GO samples suggested that the GO produced was of a similar quality as that reported in the literature. XRD analysis of the graphene suggested that the thermally reduced graphene showed high correlation with the expected data for graphene. The GO from the Tour method that was reduced using NaBH_4 also showed close resemblance to the expected results for graphene. However, all the graphene samples that were produced retained a low degree of oxygen-functionalisation as suggested by the EDX and XRD data. This outcome indicates that the method of reducing GO requires further optimisation.

Graphene nanofibres were successfully produced and the morphology of the fibres were investigated using SEM. The development of the electrospinning method of producing graphene fibres proved to be an iterative process involving the execution of multiple experiments before

arriving at the final, optimised processing and solution parameters required for the production of graphene nanofibres. These parameters were: needle gauge of 18 G, flow rate of 70 $\mu\text{l}/\text{min}$, applied voltage of 20 kV, tip-to-collector distance of 15 cm, PVA solution concentration of 12 % (wt. /vol.), and graphene concentration of 5 % (wt. /vol.) There is great potential in the study of this material as a pseudo one-dimensional material.

As mentioned, this research was the first of its kind in the laboratory; the scope of which was fairly uncharted ground for the student however the results from the experiments conducted over the one year of research provided insight into the various chemical synthesis routes of graphene and the resulting products thereof. This research also proposed a method through which graphene nanofibres and macroscopic fibres may be produced. These results may be improved upon by using this research as the foundation for further related studies.

Chapter 9 Future work

This research was the first to produce graphene fibres in Electronic Engineering at UKZN and the graphene research presented in this dissertation is also part of the early stages of graphene-related research in the Materials Science Laboratory. Already, the synthesised graphene has been used to produce graphene 100 Farad supercapacitors! It has been mentioned previously that difficulties exist in isolating graphene in its single-layer pristine form. This is one of the main obstacles in the growth of graphene related technologies. The graphene that was produced here was of a sufficiently high standard, however, there is room for improvement and optimisation of the reduction techniques. This dissertation presents various routes through which to attain graphene, and it may serve as the foundation on which to build upon further graphene related research.

The experimental chapter on the fabrication of graphene fibres was compiled in a form that will act as a guide for further research into this field of study. Since optimising the process of electrospinning proved to be a laborious, iterative procedure, this chapter will convey what has proved successful to the reader. The possible applications of these produced fibres lie primarily in the field of composite materials where the fibres may act as strengthening components, however, there is also scope for the conducting properties of these fibres to be improved upon and tuned for electrical-related applications. This would pave the way for further research to be conducted with the focus on investigating and tailoring the properties of the produced graphene fibres for specific applications.

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