Production of High-quality Few-layer Graphene Flakes by Intercalation and Exfoliation

Thesis by

Areej Abdulrahman Ali Alzahrani

In partial fulfillment of the requirements

For the degree of

Master of Science

King Abdullah University of Science and Technology

Thuwal, Kingdom of Saudi Arabia

November, 2017
The thesis of Areej Abdulrahman Alzahrani is approved by the examination committee:

Committee Chairperson: Prof. Pedro M. F. J. Costa
Committee Member: Prof. Frederic Laquai, Prof. Khaled Salama
ABSTRACT

Graphene, a two-dimensional nanomaterial, has been given much attention since it was first isolated in 2004. Driving this intensive research effort are the unique properties of this one atom thick sheet of carbon, in particular its electrical, thermal and mechanical properties. While the technological applications proposed for graphene abound, its low-cost production in large scales is still a matter of interrogation. Simple methods to obtain few-layered graphene flakes of high structural quality are being investigated with the exfoliation of graphite taking a prominent place in this arena. From the many suggested approaches, the most promising involve the use of liquid media assisted by intercalants and shear forces acting on the basal layers of graphite.

In this thesis, it is discussed how a novel method was developed to produce flakes with consistent lateral dimensions that are also few-layered and retain the expected structural and chemical characteristics of graphene. Here, the source material was a commercially available graphite-intercalated compound, also known as expandable graphite. Several exfoliation-inducing tools were investigated including the use of blenders, homogenizers, and ultrasonic processors. To aid in this process, various solvents and intercalants were explored under different reactive conditions. The more efficient approach in yielding defect-free thin flakes was the use of thermally expanded graphite in boiling dimethylformamide followed by ultrasonic processing and centrifugation. In parallel, a method to fraction the flakes as a function of their lateral size was developed. Ultimately, it was possible to obtain samples of graphene flakes with a lateral dimension of a few micrometers (<5 μm) and thickness of 1-3 nm (i.e. <10 layers).
ACKNOWLEDGEMENTS

Firstly, I would like to express my sincere gratitude to my advisor, Prof. Pedro Da Costa, for his continuous support throughout my Master’s study and related research – as well as his patience, motivation, and immense knowledge. His guidance has helped me enormously during both the experimental, and writing phases of my thesis.

Besides my advisor, I would also like to thank the other members of my thesis committee, Prof. Khaled Salama and Prof. Frederic Laquai, for their insightful comments and availability to examine this work.

My sincere thanks also go to Dr. Arnab Giri who served as the second reader of this thesis. I am gratefully indebted for his day-to-day guidance, invaluable constructive criticism and friendly advice. I am highly thankful to my colleague Nitinkumar Batra, for his help during TEM analysis and to Jasmin Smajic for his unconditional help and support. I am also very much grateful to my labmates for the stimulating discussions. With special thanks to Dr. Tamilarasan Palanisamy, Amira Alazmi and Filipa Simoes. Each of them equally contributed for me to fulfill my research project fruitfully, not to mention their gracious and pleasant company.

My special thanks to my friends in and outside of the KAUST community, for their support and encouragement. Finally, it is an honor to acknowledge my family for providing me with unfailing support and continuous encouragement throughout my years of study.
## LIST OF ABBREVIATIONS

<table>
<thead>
<tr>
<th>Definition</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>AFM</strong></td>
</tr>
<tr>
<td><strong>SEM</strong></td>
</tr>
<tr>
<td><strong>DMF</strong></td>
</tr>
<tr>
<td><strong>TEG</strong></td>
</tr>
<tr>
<td><strong>GIC</strong></td>
</tr>
<tr>
<td><strong>FLG</strong></td>
</tr>
<tr>
<td><strong>SLG</strong></td>
</tr>
<tr>
<td><strong>EG</strong></td>
</tr>
<tr>
<td><strong>TEM</strong></td>
</tr>
<tr>
<td><strong>HRTEM</strong></td>
</tr>
<tr>
<td><strong>EDS</strong></td>
</tr>
<tr>
<td><strong>DLS</strong></td>
</tr>
<tr>
<td><strong>HOPG</strong></td>
</tr>
</tbody>
</table>
**TABLE OF CONTENTS**

<table>
<thead>
<tr>
<th>TOPIC</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>EXAMINATION COMMITTEE PAGE</td>
<td>2</td>
</tr>
<tr>
<td>COPYRIGHT PAGE</td>
<td>3</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>4</td>
</tr>
<tr>
<td>ACKNOWLEDGMENTS</td>
<td>5</td>
</tr>
<tr>
<td>LIST OF ABBREVIATIONS</td>
<td>6</td>
</tr>
<tr>
<td>TABLE OF CONTENTS</td>
<td>7</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>9</td>
</tr>
<tr>
<td>LIST OF TABLES</td>
<td>14</td>
</tr>
</tbody>
</table>

**Chapter 1 - Introduction**

1.1 Carbon materials
1.1.1 Allotropes
1.1.2 Nanocarbons
1.1.3 Graphene – Structure
1.1.4 Graphene – Properties
1.2 Production
1.2.1 Physical exfoliation
1.2.2 Physico-chemical exfoliation
1.2.3 Chemical exfoliation
1.2.4 Size-fractioning

**Chapter 2 – Experimental Methods**

2.1 Materials
2.2 Exfoliation methods

2.3 Synthesis of thermally-expanded graphite (TEG)

2.4 Chemical exfoliation of TEG

2.5 Chemical exfoliation of size-fractioned TEG

Chapter 3 – Characterization Methods

3.1 Raman spectroscopy

3.2 Atomic Force Microscopy (AFM)

3.3 Electron microscopy (scanning and transmission)

3.4 Dynamic Light Scattering (DLS)

Chapter 4 – Results and Discussion

4.1 Thermally-Expanded Graphite (TEG)

4.2 Chemical exfoliation of TEG

4.2.1 Solvent-guided exfoliation using ultrasonication

4.2.2 Solvent-guided exfoliation using a homogenizer

4.2.3 Solvent-guided exfoliation using ultrasonication and an intercalant

4.2.4 Solvent-guided exfoliation using a homogenizer and an intercalant

4.2.5 Size-fractioned TEG

4.2.6 Exfoliation of the size-fractioned TEG

Chapter 5 – Final Discussion

Chapter 6 – Conclusions and Outlook

References
# LIST OF FIGURES

<table>
<thead>
<tr>
<th>Figure</th>
<th>Description</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>Figure 1.1.</td>
<td>Graphene (2D) can be the basis for other carbon materials. Left to right: Fullerenes (0D) are formed by wrapping up graphene, carbon nanotubes (1D) are formed by rolling up cylinders of graphene, and graphite (3D) is formed by stacking graphene.</td>
<td>17</td>
</tr>
<tr>
<td>Figure 1.2.</td>
<td>Mechanical exfoliation of graphene utilizing scotch tape from HOPG.</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.3.</td>
<td>The ‘honeycomb’ crystal lattice of graphene.</td>
<td>19</td>
</tr>
<tr>
<td>Figure 1.4.</td>
<td>(a) Hexagonal lattice of graphene consisting of two triangular lattices A and B, (b) the reciprocal lattice corresponding to the corners of Brillouin zone (Bz) K and K’. The a₁ and a₂ define the reciprocal lattice parameters.</td>
<td>21</td>
</tr>
<tr>
<td>Figure 1.5.</td>
<td>Mechanical routes for graphite exfoliation (Normal and Shear force application) into graphene flakes and auxiliary fragmentation route.</td>
<td>23</td>
</tr>
<tr>
<td>Figure 1.6.</td>
<td>Scotch-tape technique for the micromechanical cleavage of HOPG.</td>
<td>24</td>
</tr>
<tr>
<td>Figure 1.7.</td>
<td>Illustration of the ball mining mechanical mechanism of graphite exfoliation.</td>
<td>26</td>
</tr>
<tr>
<td>Figure 1.8.</td>
<td>In the intercalation process, guest particles (ions or molecules) are inserted between the host’s basal planes.</td>
<td>28</td>
</tr>
<tr>
<td>Figure 2.1.</td>
<td>Blender with a flask of 1.5 L capacity.</td>
<td>31</td>
</tr>
<tr>
<td>Figure 2.2.</td>
<td>Ultrasonic processor (enclosed in an acoustic box) and respective controller.</td>
<td>32</td>
</tr>
<tr>
<td>Figure 2.3.</td>
<td>(a) A rotor-stator homogenizer and (b) rotor-stator probe.</td>
<td>33</td>
</tr>
<tr>
<td>Figure 2.4.</td>
<td>A summary of the process used to produce TEG.</td>
<td>34</td>
</tr>
<tr>
<td>Figure 2.5.</td>
<td>(a) Schematic illustration for TEG exfoliation using boiling DMF, (b) Supernatant material (marked by the red square) after ultrasonication and centrifugation; (c) photo of exfoliated powder after it was dried.</td>
<td>35</td>
</tr>
</tbody>
</table>
Figure 2.6. (a) Schematic illustration for TEG exfoliation using boiling DMF and Na$_2$SO$_4$; (b) Image of the graphene aqueous solution prepared from Na$_2$SO$_4$-assisted direct exfoliation of TEG in DMF.

Figure 3.1. Different types of energy exchange processes derived from the interaction of light with matter.

Figure 3.2. (a) The Alpha 300 RA confocal Raman microscope and (b) the three lasers that equip the spectrometer.

Figure 3.3. A schematic illustration of an AFM scanning machine.

Figure 3.4. (a) A schematic illustration of the contact mode; (b) A schematic illustration of the non-contact mode.

Figure 3.5. The AFM Park-Systems XE-100.

Figure 3.6. A schematic illustration of a SEM.

Figure 3.7. The FEI QUANTA 600F microscope.

Figure 3.8. A schematic representation of a TEM.

Figure 3.9. The FEI Titan microscope.

Figure 3.10. The Zetasizer Nano DSL measuring equipment.

Figure 4.1: Summary of the process used to produce TEG.

Figure 4.2: Size distribution of the TEG dispersed in water, at room temperature.

Figure 4.3: (a) An agglomerate of TEG flakes; (b-d) Isolated TEG flakes.

Figure 4.4: (a) A flake of TEG; (b) EDS spectrum of the flake in (a).

Figure 4.5: AFM topography images of TEG flakes deposited on a silicon wafer and corresponding thickness profiles.

Figure 4.6: (a) Raman spectra of a TEG flake; (b) Peak-fitting of the 2D band.

Figure 4.7 Typical TEM images of TEG flakes. (a-b) Low-resolution TEM images of multilayer graphene (inset of (a) ED pattern of a TEG flake); (c-d) TEM image of
a multi-layer graphene flake and (e) a high-resolution image of the folding edge of a flake with outset showing dark and bright lines from the graphene layers.

Figure 4.8: Size distribution of TEG flakes exfoliated by boiling and ultrasonication in DMF.

Figure 4.9: SEM images of some TEG flakes exfoliated by boiling and ultrasonication in DMF.

Figure 4.10: (a) Exfoliated flake prepared by boiling and ultrasonication in DMF; (b) EDS spectrum of the region boxed in (a).

Figure 4.11: AFM images and respective height profiles of flakes prepared by boiling and ultrasonication in DMF.

Figure 4.12: (a) Raman map of boiled and ultrasonicated TEG flakes dispersed in DMF onto a SiO2 wafer; (b) spectrum of an individual particle.

Figure 4.13: Various flakes boiled in DMF and exfoliated (at room temperature) with a homogenizer.

Figure 4.14: (a) Flake produced with assistance of the homogenizer, in DMF; (b) EDS spectrum of the area boxed in (a).

Figure 4.15: AFM image of an isolated flake prepared by the homogenizer approach.

Figure 4.16: (a) Raman optical image of a flake exfoliated in DMF with a homogenizer and deposited on a SiO2/Si wafer; (b) Raman spectrum of the particles in (a) with the outset showing the peak fit analysis for the 2D band.

Figure 4.17: Typical SEM images of flakes prepared by intercalating Na2SO4 in boiling DMF followed by ultrasonication.

Figure 4.18: (a) Isolated flake; (b) EDS spectra for the region marked in (a).

Figure 4.19: (a) AFM images of a flake prepared by intercalating Na2SO4 in DMF; (b) corresponding height profile.

Figure 4.20: (a) Optical image of two flakes deposited on SiO2/Si wafer; (b) Raman spectra of the smaller particle boxed in (a) with the respective 2D peak fit shown in the outset (c).
Figure 4.21: Typical SEM images of the flakes exfoliated in boiling DMF with intercalant and using a homogenizer.

Figure 4.22: (a) Representative flake; (b) EDS spectrum of the area boxed in (a).

Figure 4.23: (a-b) AFM images of two typical flakes prepared by intercalating Na$_2$SO$_4$ with boiling DMF followed by homogenizer exfoliation and deposited onto a SiO$_2$/Si wafer and the corresponding thickness measurements.

Figure 4.24: (a) Optical image of an isolated particle; (b) Raman spectrum of the flake in (a); (c) Peak fitting for the 2D band in (b).

Figure 4.25: (a) Optical image of a small flake; (b) Raman spectrum of the particle in (a).

Figure 4.26: Size distribution of the size-fractioned TEG as dispersed in water, at room temperature.

Figure 4.27: Size distribution plots for TEG flakes (a) after using the solvent agitation technique (at 2500 rpm); (b) after fractionation through a 20 μm net filter (at 2500 rpm); (c) after fractionation through a 20 μm net filter (at optimal 1500 rpm).

Figure 4.28: Size distribution plot of filtered TEG with non-linear curve fitting.

Figure 4.29: Typical SEM images of TEG flakes after size-fractionation with 20 μm filter.

Figure 4.30: Typical TEM images of TEG flakes after size fractionation. (a-b) Low-resolution TEM images (the inset shows the respective ED pattern); (c-d) Medium resolution TEM images of additional TEG flakes; (e) High-resolution TEM image of the folding edge of a flake.

Figure 4.31: AFM images and respective height profiles of the size-fractioned TEG flakes.

Figure 4.32 (a) Optical microscopy image of a fractioned TEG flake; (b) Raman spectrum of the flake in (a); (c) Peak fitting of 2D band; (d-f) Spectroscopic Raman mapping of the flake in (a) with normalized intensity maps of the D, G and 2D bands, respectively.
Figure 4.33 (a) Optical microscopy image of a TEG flake; (b) Raman spectrum of the flake in (a); (c) Peak fitting of 2D band; (d-f) Spectroscopic Raman mapping of the flake in (a) with normalized intensity maps of the D, G and 2D bands, respectively.

Figure 4.34: SEM images for fractionated flakes prepared by intercalating Na₂SO₄ in boiling DMF followed by ultrasonication.

Figure 4.35: (a) Representative exfoliated-fractioned TEG flake; (b) EDS spectrum of the region marked in (a).

Figure 4.36: (a) AFM topography image of a discrete flake; (b) Height profile of the flake in (a).

Figure 4.37 Raman spectra of exfoliated-fractioned TEG flake and the peak fit of the 2D band.

Figure 4.38 Typical TEM images of exfoliated-fractionated TEG flakes. (a) Low resolution image of an isolated flake with electron diffraction pattern, inset; (b-d) High-resolution images showing that the flakes had regions that were considerably thin, just a few layers thick.
LIST OF TABLES

Table 1: The Raman spectral frequency, full-width at half-maximum (FWHM) and relative intensity for the TEG sample.

Table 2: The Raman spectral frequency, FWHM and relative intensity, for the flakes prepared using the homogenizer.

Table 3: The Raman spectral frequency, FWHM and relative intensity of a flake prepared by intercalating Na₂SO₄ in boiling DMF solvent and followed by ultrasonication.

Table 4: The Raman spectral frequency, FWHM and relative intensity of a flake prepared with intercalant Na₂SO₄ followed by homogenizer processing.

Table 5: The Raman spectral data for frequency, FWHM and relative intensity of the main bands of TEG flakes after size-fractionation.

Table 6: The Raman spectral data of frequency, FWHM and relative intensity for the flake in Figure 4.33.

Table 7: The Raman spectral data of frequency, FWHM, and relative intensity for the fractionated flakes prepared by intercalating Na₂SO₄ followed by ultrasonication.
Chapter 1 - Introduction

Carbon has many allotropes. Some of these have been known for centuries (e.g. diamond) but others were only discovered more recently (e.g. fullerenes). Graphene, the unit layer of graphite, is the most popular member of what is today denominated 2D materials family. Isolated in 2004 [1], graphene has gained increased attention from the scientific community because of its outstanding electrical, chemical, mechanical, thermal and optical properties, amongst others. It is therefore not surprising that there have been numerous propositions to translate those properties into useful technologies for Mankind.

In order to put the thesis work into context, this first Chapter discusses the relevant knowledge background of graphene materials, touching upon carbon allotropes, as well as the history, properties and production of graphene.

1.1 Carbon Materials

1.1.1 Allotropes

The list of known solid carbon allotropes is remarkably extensive and ranges from diamond to fullerenes [2]. Classically, the two most important members of this family were diamond and graphite.

*Diamond:* this allotrope has several impressive features such as high hardness, resistance to corrosion. In diamond, the C atoms are covalently bonded to form a 3D crystal lattice. Its bonds are characteristically of sp³-hybridization type which justifies their high directionally and overall hardness of this material. While electrically insulating, diamond can be doped with B or N to yield p- and n-type materials. Diamond has been mined for millennia but in the last decades it
was possible to develop artificial, industry-grade diamonds through processes such as chemical vapour deposition (CVD) or detonation [3]. Man-made diamonds are used mainly in industrial machinery such as blades [4]. Nanodiamond has also been proposed as an excellent active material for bio-sensors [5].

*Graphite*: this allotrope has been used for centuries, in particular as pencil leads. Differently from diamond, it is made of stacked layers of carbon atoms arranged in a honeycomb-fashion. Graphite is a naturally formed crystalline carbon material bearing a hexagonal lattice arrangement belonging to space group P6₃/mmc [6]. While it has been mined for long time, with ores varying in purity and degree of structural order, Mankind has discovered how to synthetically control its production. Varied sources can be used to this effect such as pitch-coke, a by-product from oil refineries. The graphite building block (graphene) looks like an enormous aromatic macromolecule where bonding amid the carbon atoms entails sp³ hybridized orbitals. The superfluous electrons in every carbon atom enter into the delocalized p-π symmetry’s orbital, generating weak van der Waals forces between the planes. Electrically, graphite behaves as a semi-metal with an almost filled π-valence band that overlaps into the virtually void π*-conduction band in specific directions in reciprocal space. Its layers are stacked together with spacing of approximately 0.335 nm. As it will be explained later, this allows for technologically relevant phenomena such as the intercalation of atoms and molecules between them.

**1.1.2 Nanocarbons**

Graphene can be seen as the building block of not just graphite but also of other carbon structures such as fullerenes and nanotubes, as shown in Figure 1.1 [7]. This attests to the flexibility of C
forming different types of nanoscaled particles based on the way the graphene layer (or strip) is manipulated.

**Fullerenes**: in 1985, Robert Curl, Richard Smalley and Harold Kroto discovered the fullerenes (0D) [8], proposing a C\(_{60}\) molecule with the shape of a ball. Nicknamed for that reason as a “Bucky-ball” (where bucky derives from Buckminster Fuller, an architect/designer of the 20\(^{th}\) century), it is composed of a sectioned graphene sheet that has been curved and where 12 pentagons are included to close the curvature into a sphere. The family of fullerenes is today extended in number with examples ranging from C\(_{20}\) to C\(_{540}\), and beyond.
Figure 1.1. Graphene (2D) can be the basis for other carbon materials. Left to right: Fullerenes (0D) are formed by wrapping up graphene, carbon nanotubes (1D) are formed by rolling up cylinders of graphene, and graphite (3D) is formed by stacking graphene [7].

Carbon nanotubes: shortly after the report on fullerenes discovery, Sumio Iijima made the first structural description of the carbon nanotube (CNT) [9]. While these had been previously observed, the intentional synthesis and structural analysis of multi-walled CNTs came at a time when fullerenes were on everyone’s mind. Here, when the graphene sheet is rolled-up, a tubular shape is originated and, depending, on the number of concentric sheets the nanotubes vary from multi- to single-walled. These nanoparticles are several micrometers long and some nanometers in diameter. With the increasing volume of research done from the 90’s onward, several hybrid structures have been produced. One such are the so-called carbon nanobuds, single-walled CNTs that are decorated with covalently-bounded fullerenes along their length [10][11].

Graphene: many teams studied graphene, going all the way back to the late 1940’s [12] [13] [14]. According to Peierls, several scientists initially thought that isolation of graphene was thermodynamically forbidden [15]. Nevertheless, Novoselov and Geim (who won the Nobel Prize in Physics in 2010) proved this wrong as they conducted the first isolation of graphene using the mechanical exfoliation technique, later to be known as “the Scotch-tape technique” [16]. Simple and affordable, this consists in applying an adhesive tape to a highly oriented pyrolytic graphite (HOPG) crystal that, when detached, can peel off some graphene flakes, as shown in Figure 1.2. These tiny particles are then deposited onto a SiO₂ substrate.
Graphene is the thinnest 2D material that has been isolated so far. It is also one of the lightest material that has been discovered [18] and has attracted significant attention due to its unique electrical [1], mechanical [19] and thermal [20] properties. This mono-atomic sheet is integrally made-up of C atoms that are connected via sp$^2$–type bonds with the C-C distance being 0.142 nm [18]. The hexagonal-type lattice is schematically shown in Figure 1.3.
1.1.3 Graphene - Structure

As mentioned above, graphene is a single layer of sp²-hybridized C atoms with a hexagonal crystal structure with a basis of two C atoms per unit cell. This honeycomb-type lattice presents unfilled π-orbitals above and below the plane of the C sheet. Morphologically, a free-standing single-layer graphene sheet shows ripples, as these are known to energetically stabilize it [22]. Strictly, graphene is the term of the monolayer of C but literature often refers to it in the broader sense, i.e. also including the “bi-layer” (where two monolayers are stacked) or “few-layer” (where commonly the number of stacked C layers is below ten) [15]. Monolayer graphene usually exists in rippled form without stacking of layers, while the bilayer and few-layer graphene have several different types of stacking sequences (AAA, ABA or ABC).

From the perspective of its electronic structure, two triangular sub-lattices are needed to construct the graphene (Figure 1.4a). The lattice vectors can be written as:

\[
\begin{align*}
\mathbf{a}_1 &= \frac{a}{2} (3, \sqrt{3}) \\
\mathbf{a}_2 &= \frac{a}{2} (3, -\sqrt{3})
\end{align*}
\]  

(1.1)

Where a ≈1.42 Å represents the distance of a C-C bond in graphene. The crystal structure of graphene can be described by the smallest unit possible known as the unit cell, which comprises of one atom from each of the interlinked sub-lattices [15]. Similarly, the reciprocal-lattice vectors are given by:
\[ a_1 = \frac{2\pi}{2a} (1, \sqrt{3}) \quad a_2 = \frac{2\pi}{2a} (1, -\sqrt{3}) \] (1.2)

In reciprocal space, the particular points are classified as \( K, K', M \) and \( \Gamma \) analogous to the corners, edge and center of the first Brillouin zone, respectively. The two points \( K \) and \( K' \) are also known as the Dirac points. Their points in momentum space are:

\[ K = \frac{2\pi}{3a}, \frac{2\pi}{3\sqrt{3}a} \quad K' = \frac{2\pi}{3a}, -\frac{2\pi}{3\sqrt{3}a} \] (1.3)

\[ \text{Figure 1.4. (a) Hexagonal lattice of graphene consisting of two triangular lattices A and B, (b) the reciprocal lattice corresponding to the corners of Brillouin zone (Bz) K and K'. The } a_1 \text{ and } a_2 \text{ define the reciprocal lattice vectors.} \]

1.1.4 Graphene - Properties

Electrical properties: graphene shows a remarkable mobility of the electrons, especially at room temperature. The mobility of these electrons does not depend on temperature especially between 10 K and 100 K. Graphene has less resistivity than silver but the charge transport is significantly affected by the presence of defects and contaminants such as oxygen or adsorbed water molecules.
Mechanical properties: graphene is one of the strongest materials ever been studied by Man, having a tensile strength of 130 GPa [12] and a Young’s modulus of 1 TPa. The stiffness was determined to be 0.5 TPa [19]. Furthermore, a large angle bent can be achieved elastically making it a very promising candidate for applications such as resonators and flexible electronics. What’s more, a good carrier mobility is retained even when there is extreme deformation.

Thermal properties: measurements on thermal conductivity show that graphene has a high thermal conductivity at room temperature, ~ 6000 W/m.K [20, 23]. However, thermal transport can be affected by the number of layers. Optothermal Raman studies show that an increasing number of planes leads to the decrease of thermal conductivity [24, 25].

1.2 Production
As the main focus of this thesis is the large-scale production of FLG flakes, the various methods available to grow/produce graphene are presented hereafter.

Several techniques have been developed with the promise to produce graphene flakes in large-scale. These can be divided into bottom-up and top-down processes [26]. The bottom-up methods depend on chemical reactions of molecular building blocks to produce covalently bonded two-dimensional carbon networks [27]. Amongst them are epitaxial growth (sublimation of SiC) and chemical vapor deposition (CVD) both of which can produce high-quality graphene. The structural quality of the produced graphene is such that can be used in electronic devices. However, these substrate-based methods have limited scope for large-scale production and are rather costly. On the other hand, top-down methods derive mainly from the exfoliation of graphite [26]. Besides less expensive, their scale-up is feasible. In the exfoliation route, two types of mechanical paths are
used: normal and shear forces (Figure 1.5). For instance, a normal force can be utilized when peeling successive layers of graphite and has been notably exploited in the Scotch-tape technique [1]. On the other hand, it is possible to exploit the self-lubricating capability of graphite to laterally peel off the layers.

![Image of normal force, shear force, and fragmentation]

**Figure 1.5.** Mechanical routes for graphite exfoliation (normal and shear force application) into graphene flakes and auxiliary fragmentation route [27].

*Fragmentation:* besides the exfoliation resulting from the action of normal and lateral forces, fragmentation is another auxiliary route during the process, as shown in Figure 1.5. If the applied forces are large enough, the exfoliated fragments may break up into smaller constituents [27]. In fact, the fragmentation has a two-fold effect: first, it reduces the lateral size of the graphene flakes (but this may not be always desired…); second, it assists the exfoliation as the smaller the flakes, the easier it becomes to exfoliate them. Fragmentation is also necessary to achieve size-fractioning
of flakes, as described further on in this thesis. In the following sections, the exfoliation methods have been divided into physical and chemical approaches.

1.2.1 Physical exfoliation

Micromechanical cleavage was the first method to be successfully used to isolate graphene [28]. Also known as the “Scotch-tape” approach, one applies the tape on the surface of a highly oriented pyrolytic graphite (HOPG) monolith and exerts a normal force to detach it. By replicating this action several times, the peeled graphite flakes become thinner and thinner, eventually originating a single layer of graphene (Figure 1.6). While the material obtained is of high-quality, mechanical exfoliation proved to be costly, time consuming and labor-intensive. Thus, it has been limited to laboratory research because it is not feasible for scale-up production.

![Figure 1.6. Scotch-tape technique for the micromechanical cleavage of HOPG [27].](image-url)
1.2.2 Physico-chemical exfoliation

Liquid-phase exfoliation: assisted by ultrasonication [29], this is a process that was initially used in 2008 [30]. In the original report, graphite powder was added to an array of different organic solvents including N-methylpyrrolidone (NMP) and N, N-dimethylformamide (DMF), followed by steps of sonication and centrifugation. The final product was the isolation of FLG flakes launching a new panorama on large-scale and low-cost industrial production of graphene. Still, one of the issues was to achieve stable suspensions. Most of the produced samples had low concentration of graphene, at 0.01 mg mL\(^{-1}\) [30]. This is far from what is requested in an industrial setting. Several other studies have followed with the aim of increasing the concentration. These suggested the use of surfactants, polymers or the utilization of solvent exchange methods [31]. Pertinently, it has been reported that the concentration of graphene dispersions produced by liquid-phase exfoliation is dependent on the solvent used, in particular its surface tension [27, 32].

Ball milling: this is one technique which is common in the powder production industry. The mechanism of graphene exfoliation during ball milling is illustrated in Figure 1.7. Shear force is the primary route for the layer peeling and results in the production of large-sized graphene flakes [32]. However, a secondary route involves the collision of the rolling balls with the graphitic flakes. Large sections are thereby fragmented into smaller units, potentially even obliterating the crystalline structure and generating amorphous carbon or non-equilibrium phases. Therefore, when using this method, it is advisable to reduce the secondary effect in order to achieve high quality and large-sized structural graphene [27]. Recently, scientists have utilized graphitic planetary ball milling in wet-state for graphene production. During this wet process, the graphite is dispersed in
selected solvents such as DMF, tetramethylurea and NMP to match the surface energy and overcome van der Waals forces of contiguous graphene flakes.

**Figure 1.7.** Illustration of the ball mining mechanism of graphite exfoliation [27].

### 1.2.3 Chemical exfoliation

Experimentally, there are two possible methods that a molecule may react and interact with graphite molecule to form a novel compound [33]. First, the molecule may form covalent bonds with carbon atoms. The reactants interrupt the aromatic structure and produce non-conducting graphite products where the mono-atomic carbon layers are crumpled rather than planar. Second, the reacting molecule may form polar interactions that involve graphite \(p-\pi\) connection. The reacting molecules are then held within the graphite without upsetting the aromatic arrangement of the honeycomb-type lattice. This approach is dependent on the capability of intercalating atoms or molecular species between the unit layers of graphite.
Hummer’s method: this is the oldest approach wherein graphite is oxidized through the use of concentrated acids or other strongly oxidizing agents [34]. Classically, it entails mixing graphite powder with sodium nitrate in sulphuric acid at low temperatures (between 0 °C and 5 °C). This is then dissolved with potassium permanganate, keeping the temperature low. The mixture is diluted in water and heated to 98 °C, following which the reaction is terminated using hydrogen peroxide and purified with hydrochloric acid [34]. Some of the benefits of the Hummer’s method are the fairly quick reaction and high efficiency, as well as reduced fog production [35]. However, there are drawbacks such as safety issues, the large size distribution of the produced flakes and a high concentration of functionalization/defects induced into the graphitic planes and edges [36]. The wide range of defects and oxygen-containing functional groups density in the oxidized nanosheets influences the chemical, physical, electrical, and optical characteristics of the graphite oxide and limits its applications [35]. In fact, and as reported in [37], there is a clear effect on supercapacitor performance with varying degrees of oxidation, morphology and electrochemical response observed when comparing graphite oxidized and reduced differently. Amira et al. also demonstrated that tailoring of the type and density of functional groups may be required to adapt the graphene oxide to the desired applications [38][39].

Intercalation: this approach refers to the insertion of species including ions, atoms or molecules into the inter-planar spaces of the graphene lamellas without destroying or functionalizing the honeycomb lattice, as shown in Figure 1.8. The process is essentially reversible through appropriate chemical or thermal treatments. Generally, for purposes of intercalation of foreign species, graphite has been considered one of the best host materials known. In fact, the first report of this kind dates from 1926 [33] and today, the resulting materials are referred to as graphite
intercalation compounds (GIC). The intercalation process weakens the inter-planar forces and aids in the partition of the layers. It is accepted that the order of arrangement, bond distances and bond direction may become distorted, but the lamellar uniqueness of the host remains unchanged.

![Figure 1.8](image)

**Figure 1.8.** In the intercalation process, guest particles (ions or molecules) are inserted between the host's basal planes [40].

### 1.2.4 Size-fractioning

Size-sorting of exfoliated graphene flakes has motivated much research in recent years. Properties may change depending on shape and size of the flakes. Also, there are applications that require a control over the particle size and/or the size distribution. For instance, large-area graphene sheets are used when fabricating optoelectronic devices and nanopore membranes [41]. On the other hand, small area graphene flakes commonly have more functional groups attached and are therefore suitable for bio-sensing and drug delivery applications. While the reduction of graphene oxide is one of the most reliable methods to potentiate the scale-up production of flakes [42], a broad size distribution is observed upon the synthesis and subsequent product processing. For this
reason, it is advisable to plan for their size-sorting (or fractioning) to obtain well-defined areas and narrow size distributions. Accordingly, several attempts have been made to fraction FLG samples (whether derived from GO or other production method) and include, amongst other methods, using pH-assisted fractionation [43], polar solvent agitation [44], density gradient centrifugation [45], track-etched membrane filtration [46] and circular motion of solvent [47]. While interesting, these processes are still unable to result in a satisfactory outcome in terms of scalability, as the time required for processing and the huge amounts of solvent used would be prohibitive. Thus, an effective method to fraction FLG products remains to be developed.
Chapter 2 – Experimental Methods

2.1 Materials

- Expandable graphite (Asbury Inc., grade 3772, particle size 80% >300 µm, 99 at% C, expansion ratio minimum 270, pH range of 5-10)
- Distilled water (Milli-Q water, 18.2 MΩ.cm@25 °C)
- Dimethylformamide (DMF, Fisher Scientific, assay ≥99.5%, CAS68-12-2)
- Na₂SO₄ (Sigma-Aldrich, ≥99.99% trace metals basis, form: powder, 2.68 g/ml, m.p.: 884 °C, CAS: 7757-82-6)
- HNO₃ (Sigma-Aldrich, b.p.: 122 °C, 1.413 g/ml, CAS 7697-37-2)
- Ethanol (VWR, 0.81 kg/L, CAS: 64-17-5)

2.2 Exfoliation methods

**Blender:** blending is an intensive mixing process that has been in existence since 1922, invented by Stephen Poplawski [48]. This is one of the simplest forms of mixing two or more substances. These may exist as particulates and/or liquid, thereby resulting in what may be described as solid (or liquid) blending or liquid-solid blending. Normal tumble blending of freely viscous materials is characterized by a gentle mixing action. Conversely, it is necessary to use an internal agitator for materials that tend to lump-up or require high intensity blending [48]. In Figure 2.1, the blender used to mix carbon particulates and solvents is shown.
Figure 2.1: Blender with a flask of 1.5 L capacity.

Ultrasonic processor: this is a versatile and relatively simple method of exfoliating graphite in liquid phase. This technique, used in a number of material synthesis methodologies, involves both physical and chemical mechanisms. The physical phenomenon is referred to as cavitation (i.e. generation and collapse of heated air bubbles) and is capable to initiate a chemical reaction. The chemical phenomenon is referred to as nebulization – this will foster the reaction within the heated bubbles. As a result, highly reactive substances such as peroxides and molecular radicals can be produced. Additionally, there is an associated mechano-chemical effect which is known to assist in the exfoliation of layered materials such as graphite [49]. In Figure 2.2, the ultrasonic processor used to exfoliate the graphitic particles in this work is shown.
**Homogenizer:** this equipment is often seen as an advanced version of a blending machine, designed for use in industry as shown in Figure 2.3. Unlike a simple kitchen blender (such as the one in Figure 2.1), the working mechanism of a homogenizer is rather complicated. As its derived verb, "homogenizing" suggests that this tool is capable of mixing, stirring, dispersing, and emulsifying materials [50]. The equipment works by injecting samples into liquid medium through a narrow escape. Multiple forces which include turbulence, cavitation and high pressure, all act on the sample to create uniform dilutions of a material with pre-determined size that is suspended in an appropriate diluting agent. The machine uniformly macerates or crushes the sample so that its constituents disperse throughout the diluting agent in the form of minute fragments. During this
process, an underlying assumption is that only the physical and not the chemical properties of the samples change.

Figure 2.3: (a) A rotor-stator homogenizer and (b) rotor-stator probe [51].

An example of a lab-scale homogenizer is shown in Figure 2.3 (a). The equipment has a rotating shaft (rotor) and a stator. The tip of the shaft is machined to have slots while the rotor doubles as a blade, as illustrated in Figure 2.3 (b). An appropriately sized sample volume is forced up from the dispersion into the stator by the rotating blade [52]. Here, the sample is centrifugally ejected through the slots in a pump-like style. Due to the high speed of the blade, the material is rapidly cut and disintegrated by a mix of strong turbulence, shearing and cavitation forces, all taking place inside the narrow space that separates the rotor from the stationary stator.
2.3 Synthesis of thermally-expanded graphite (TEG)

1 g of expandable graphite (EG) was placed in a 150 ml quartz crucible and covered with a lid. The content was heated in a muffle furnace at 1050 °C for about 30 seconds. After this thermal shock, the crucible was removed with a tong and allowed to cool for 10 min. 1 g of the EG sample was put in a blender flask (ALSAIF-ELEC, model Hummer, 1500 W) and 500 ml of distilled water poured into it. The high-speed mixing action of the blender helped in the process of shear exfoliation of the EG. After 30 min, the content of the flask was filtered using a filter paper (Whatman, size 150 mm). The powdered product was then frozen at -80 °C for 24 hrs. Subsequently, it was dried in a freeze-dryer (under 0.008 mPa at -87 °C for 48 hrs), to produce thermally-expanded graphite (TEG) powder. A summary of these processes is shown in Figure 2.4.

Figure 2.4: A summary of the process used to produce TEG.
2.4 Chemical exfoliation of TEG

**Solvent-guided exfoliation using ultrasonication:** the previously obtained TEG was further exfoliated (Figure. 2.5 (a)). In a typical synthesis, 50 mg of TEG powder were added to 200 ml of DMF. The mixture was then vigorously stirred and heated-up for 4 hrs at 153 °C (i.e. boiling point of DMF), as shown in Figure. 2.5 (a). This was followed by 10 min of sonication at 100 W (Cole-Parmer ultrasonic processor). The resulting product was an ink-like graphene dispersion which was centrifuged at 10,000 rpm for 5 min (Hettich, Universal320). The purpose of this step was to precipitate the remaining large aggregates of graphite (Figure. 2.5 (b)). The supernatant was extracted and passed through a Whatman filter paper. Finally, the filtered material was dried overnight in a vacuum oven at 60 °C resulting in the powder shown in Figure. 2.5 (c).
Figure 2.5: (a) Schematic illustration for TEG exfoliation using boiling DMF; (b) Supernatant material (marked by the red square) after ultrasonication and centrifugation; (c) photo of exfoliated powder after it was dried.

**Solvent-guided exfoliation using a homogenizer:** the above process was repeated with the exception that a homogenizer (at 20,000 rpm for 5 min) was used instead of the ultrasonic processor.

**Solvent-guided exfoliation using ultrasonication and an intercalant:** Na$_2$SO$_4$ was used as an agent to further intercalate and exfoliate the TEG. In a typical synthesis, 50 mg of TEG and 25 mg of Na$_2$SO$_4$ were added to 200 ml of DMF. The mixture was then vigorously stirred and heated-up for 4 hours at 153 °C (*Figures. 2.6 (a) and (b)*). This was followed by 10 min of sonication at 100 W. Next, the dispersion was washed with water to remove the residual salt and centrifuged at 10,000 rpm for 5 min to deposit the larger aggregates. The supernatant was collected, filtered and dried overnight in a vacuum oven at 60 °C.

**Solvent-guided exfoliation using a homogenizer and an intercalant:** the above process was repeated with the exception that a homogenizer (at 20,000 rpm for 5 min) was used instead of the ultrasonic processor.
Figure 2.6: (a) Schematic illustration for TEG exfoliation using boiling DMF and Na₂SO₄; (b) Image of the graphene aqueous solution prepared from Na₂SO₄-assisted direct exfoliation of TEG in DMF.

2.5 Chemical exfoliation of size-fractioned TEG

Size-fractioning of TEG: 1 g of TEG was blended for 15 min and then homogenized at 25,000 rpm for 8 min. Next, the product was repeatedly washed with alternating 40 ml HNO₃ and hot water (to remove impurities). After filtering (Whatman No. 4 filter paper), the resulting powder material was collected and freeze-dried (at -80 °C) for three days. Afterwards, 100 mg of this material was dispersed in 500 ml of ethanol and passed through a 60 µm or 20 µm Nylon mesh filter (Filter type: 60 µm NY60, 20 µm NY20, MILLIPORE) while being subjected to slow stirring.
(to minimize clogging of the filter). Following the complete filtration of the dispersion, the liquid containing the small-sized flakes was homogenized at 25,000 rpm for 8 min. After a rest period of 2 hrs, the supernatant was collected (through decantation), filtered and dried for 4 hrs in a vacuum oven at 70 °C.

**Solvent-guided exfoliation of size-fractioned TEG using ultrasonication and an intercalant:** 50 mg of the size-fractioned TEG and 25 mg of Na₂SO₄ were added to 200 ml of DMF. The mixture was vigorously stirred and heated-up for 4 hrs at 153 °C. This was followed by 10 min of sonication at 100 W. Next, the dispersion was washed with water to remove residual salt and centrifuged at 10,000 rpm for 5 min (to induce the deposition of aggregates). The supernatant was collected, filtered and dried overnight in a vacuum oven at 60 °C.
Chapter 3 – Characterization Methods

Graphene has a simple atomic structure. Despite this, it is both difficult to make it uniformly and characterize its properties. In fact, there are no specific standards in the industry for properly quantifying the relevant properties of this material. For a complete analysis of the materials produced in this thesis, several tools were employed, as described below.

3.1 Raman spectroscopy

Raman spectroscopy is pillared on the concept of scattering light. If one were to shine light of a certain frequency onto a thick material, one expects to just see that light reflected from it or no light at all [53]. However, with the assistance of a Raman spectrometer, one might identify that a minute fraction of the dispersed light has a different frequency. This change, which underpins Raman scattering analytical methods, is due to variations in energy of the light-wave after its interaction with materials, namely at the level of molecular vibrations. Effectively, in light-matter interactions, four different types of energy exchange are possible: absorption, spontaneous emission, stimulated emission and Raman scattering (Figure 3.1) [18]. From Figure 3.1, it is taken that every atom or molecule has a unique set of vibration energy levels. Consequently, the photons emitted have different wavelength shifts. Raman spectroscopy entails collecting and analyzing these wavelength fluctuations and using them to ascertain the constituents and structure of the sample material. From this perspective, different peaks in the spectrum infer different Raman excitations.
Figure 3.1: Different types of energy exchange processes derived from the interaction of light with matter.

The Raman spectrometer used in this thesis is a WITec Alpha 300RA (Figure 3.2 (a)). It is equipped with three lasers: DPSS 488 nm, Nd:YAG 532 nm, and He:Ne 633 nm, as shown in Figure 3.2 (b). Here, the Nd:YAG 532 was employed. This equipment integrates a confocal microscope system for high quality chemical mapping studies. It also includes an atomic force microscope set-up that enables correlated analysis of surface structure and composition [1].
Figure 3.2: (a) The Alpha 300 RA confocal Raman microscope and (b) the three lasers that equip the spectrometer.

3.2 Atomic force microscopy (AFM)

The AFM is a versatile characterization tool that can ultimately provide near-atomic resolution surface images of nanostructures. Underpinning the workings of AFM is the attractive force exerted between the sample and a sharp tip, placed at the end of a cantilever, which is used to scan the surface of the sample (Figure 3.3). Generally, the cantilever is approximately 100 μm long, 10 μm wide and 1 μm thick and its free-standing end contains a sharp tip made of Si. An electrostatic attraction becomes dominant when the distance between the tip and the surface of the sample is short. However, as the cantilever inches closer to the surface, in such a manner that the tip makes contact with it, a counter repulsive force emerges and makes the cantilever deflect away from the
surface [53]. The AFM uses a beam of light from a photodiode detector to sense these cantilever deflections, towards or away from the sample. In the course of deflecting an incident beam away from the top of the cantilever, small changes take place in the direction of the reflected beam. In this case, the photodiode detector is responsible for tracking these changes. Thus, if an AFM proceeds over a raised sample surface, the consequential cantilever deflections as well as the shift in the direction of the light are recorded by the photodiode detector. Further to this, by allowing a feedback loop to control the height of the tip above the sample, i.e. by maintaining a constant laser position, an AFM can accurately image the topography of the sample.

![Figure 3.3: A schematic illustration of an AFM scanning machine [53].](image)
The AFM has two major imaging modes (Figure 3.4): contact and non-contact.

**Contact Mode:** in this mode, which is the most commonly used, the tip makes “soft contact” with the sample surface and the study of the sample’s topography is facilitated by the repulsive force created vertically between the sample and the tip. The contact mode is the simplest, albeit also most aggressive, imaging mode. This means that chances of damaging a soft sample are high while the tip is also at risk when a hard sample is used. Thus, the mode is most preferable in an air or fluid environment.

![Contact Mode](image1)

![Non-contact Mode](image2)

**Figure 3.4:** (a) A schematic illustration of the contact mode; (b) A schematic illustration of the non-contact mode [53].
**Non-Contact Mode:** in this mode, the setup traces surface topography by utilizing the attractive atomic force in a considerably larger distance between the tip and the sample surface than that used in contact mode. As the tip never touches the surface of the sample, the non-contact mode is highly recommended for soft samples. The chances of damaging both the tip and the sample surface are minimal [53]. In this work, most of the analysis carried out by AFM was undertaken using the non-contact mode. **Figure 3.5** illustrates the AFM Park-Systems XE-100 equipment used.

**Figure 3.5**: The AFM Park-Systems XE-100.
3.3 Electron microscopy (scanning and transmission)

While an ordinary light microscope uses visible light to image specimens, the scanning and transmission electron microscopes use accelerated electrons. Their significantly lower wavelength makes it possible to determine features in specimens with a resolution that is 1000 times better than the light microscope.

**Scanning electron microscopy (SEM):** a schematic diagram of a SEM is shown in Figure 3.6. The electron gun generates a beam of electrons via a thermal emission source such as a heated tungsten filament. The energy of these particles may be as low as 100 eV or as high as 30 keV. The imaging electrons travel down the column and are focused into a small beam by a system of electromagnetic lenses. Thereafter, scanning coils, found towards the end of the column, focus and position the beam of electrons onto the sample surface to be analyzed. The electron beam is scanned in a rectangular manner over the surface for imaging. It is also possible to focus the beam onto a single point or scan it along a line for X-ray analysis [54].
For a SEM image to be created, the incident beam is scanned across the sample’s surface and the subsequently emitted electrons are collected by an electron detector (for every single point on the scanned surface). The strength of the emitted electron signals is output as brightness on the display monitor. If one were to synchronize the position in the image scan with that of the scan of the incident electron beam, then the display would output the morphology of the sample surface area. On the same note, the ratio of the image display size to the sample area scanned by the beam gives the magnification value of the image.

For the purpose of this work, a FEI QUANTA 600F (Figure 3.7) was used, along with a detector for secondary electrons (SE). These are lower-energy particles emitted by the specimen and are
attributed to inelastic scattering [56]. Besides the SE detector, the QUANTA 600F is fitted with a tungsten filament (which provides the electron beams needed during imaging of the samples), a backscattered electron detector (to facilitate mean atomic number imaging), and an energy-dispersive X-ray spectroscopy (EDS) detector, with which it is possible to chemically analyze the sample [57].

Transmission electron microscopy (TEM): a schematic view of a TEM is given in Figure 3.8. Just as the SEM, the source of electrons is located in the upper part of the column and electromagnetic lenses are used to focus the charged particles into a beam. Contrastingly to the
SEM, the electrons are not converged and the surface scanned to form the image. Instead, in TEM, the electrons transverse the thin sample and are collected on a fluorescent screen (or another registering device). For this, a second pair of lenses casts either an image of the specimen, or a diffraction pattern, using the transmitted electrons.

Figure 3.8: A schematic representation of a TEM [58].

In this work, an FEI Titan ST 80-300 was mainly used (Figure 3.9). This instrument has an electron gun that emits and accelerates electrons to energies between 80 keV and 300 keV. This equipment is equipped with an EDS detector.
Energy dispersive X-ray spectroscopy (EDS): this technique is used to analyze the local chemical composition of a material inside an electron microscope. Its main principle of operation is the interaction between electromagnetic radiation and matter, in particular the analysis of the X-rays emitted by the sample after being hit with charged particles. In the current study, a Si drift detector was used in both types of electron microscopes (SEM and TEM).
3.4 Dynamic light scattering (DLS)

DLS is a very useful tool to characterize the size of graphene particles [59]. In this technique, a laser illuminates the particles in suspension and measures intensity fluctuations of the scattered light. **Figure 3.10** shows the equipment used, namely the Zetasizer Nano [60]. For this work, the graphene samples were suspended in water or a selected organic solvent. The rationale for using water is that it has a well-characterized refractive index. However, graphene is hydrophobic and does not form a stable dispersion in pure water. On this basis, an organic solvent is included – its refractive index should be almost identical to water and with the ability to stabilize graphene particles. After the sample is inserted into the cell area, a monochromatic laser light source is passed through it. The outcome is that the light is scattered in all directions as it strikes the graphene particles. It experiences either constructive or destructive interference resulting in light and dark regions when focused on a screen. The light and dark regions form a speckled pattern. The process is repeated over several short time intervals and the resulting data analyzed using scattering theory (to establish the particle size distribution).
Figure 3.10: The Zetasizer Nano DSL measuring equipment.
Chapter 4 – Results and Discussion

4.1 Thermally-Expanded Graphite (TEG)

The initial material used in this thesis, i.e., with which all the below exfoliation and fractioning procedures were tested on, was a thermally-expanded graphite (TEG) powder. The expansion procedure was previously optimized in the Laboratory for Carbon Nanostructures (LCN) by Dr. Shashikant Patole [61]. The process of producing the TEG is schematized below, **Figure 4.1**.

![Figure 4.1: Summary of the process used to produce TEG.](image)

On completion of the procedure above, the characterization of the product was carried out. First, the size distribution of the particles was studied with a particle size analyzer. This equipment uses laser scattering to estimate the lateral size of the TEG flakes when dispersed in solvents (**Figure 4.2**). The analysis of the curve shows that it has a unimodal distribution with a mean peak at 56 µm. The percentile 50% is at 53 µm while the percentile 80% is at 98 µm. Overall, it can be stated that the lateral size for the majority of the particles lies in the interval of 45-75 µm.
Knowing the average size of the particles, the morphology of the TEG flakes was analyzed. Figure 4.3 shows typical SEM images of isolated flakes. These were between 20-50 µm and presented some of the distinguishable features of graphite such as jagged edges. It is also clear that the flakes are composed of many layers of graphene. Often they are crumpled and show sections that are partially exfoliated. At some instances, particles of another material were seen (possibly the intercalant salt used to make the TEG, not shown).
In addition to imaging, the SEM was also used to confirm the chemical composition of the flakes. Figure 4.4 shows the results of the EDS analysis of an isolated TEG flake. When placing the converged electron probe on the particle, only the carbon element was identified.

Despite the lack of surface regularity across the individual flakes, some parts could be analyzed with AFM. The purpose of this was to understand the size, surface topography and, more importantly, the average thickness of the flakes. In Figure 4.5, a typical image is showed along with the height profiles in two different regions of a flake. The brighter areas correspond to points that are thicker in the flake. From the various profiles taken, the heights varied from 80 to 100 nm. The surface topography is expectedly rough due to graphene folds, partially exfoliated regions, etc. As for the lateral size, this matched well the information previously extracted from the size analyzer and the SEM (range of 20-70 µm).
While the above characterization provided information on size and morphology of the flakes, their structure and texture were studied with Raman spectroscopy. In this, it is important to look at the frequency, relative intensity and width of the characteristic bands. **Figure 4.6** illustrates the typical Raman spectrum of a TEG flake. In it, the three bands that define graphitic materials are present, namely the D, G and 2D. More details are provided in **Table 1**.
Figure 4.6: (a) Raman spectra of a TEG flake; (b) Peak-fitting of the 2D band.

The degree of structural order of the flake probed in Figure 4.6 is relatively high, illustrated from the $I_D/I_G$ ratio of 0.1 and the narrow G-band. For graphene, it is also common to state the $I_{2D}/I_G$ ratio. While this is particularly relevant for CVD-grown layers, for exfoliated flakes, it is harder to interpret this information. Nonetheless, for reference, the value found was 0.26. Further to this, the deconvolution of the 2D band was carried out to show its lack of symmetry. According to some authors [62], this is indicative of the presence of multilayers of graphene.

Table 1. The Raman spectral frequency, full-width at half-maximum (FWHM) and relative intensity for the TEG sample.

<table>
<thead>
<tr>
<th>BAND</th>
<th>FREQUENCY (CM$^{-1}$)</th>
<th>FWHM (CM$^{-1}$)</th>
<th>RELATIVE INTENSITY</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1343</td>
<td>57</td>
<td>7%</td>
</tr>
<tr>
<td>G</td>
<td>1578</td>
<td>23</td>
<td>100%</td>
</tr>
<tr>
<td>2D</td>
<td>2694</td>
<td>52</td>
<td>29%</td>
</tr>
</tbody>
</table>
The microstructure of the flakes was further analyzed with TEM. A typical TEG particle can be seen in the low-/medium-resolution TEM images in Figures 4.7 (a-b). Whilst the particle is transparent, folds and other surface features responsible for roughness are visible. To look into the thickness of the flake and observe the stacking order of the graphene layers, high-resolution imaging was performed, as shown in Figures 4.7 (c-d). The intensity line profiles taken from the outset of Figure 4.7 (e) revealed the presence of an average of 200-300 layers of graphene, which implies a flake thickness of approximately 80-100 nm. This agrees well with the AFM height profile measurements. Electron diffraction patterns were also taken for this sample. An example is shown in Figure 4.7 (a, inset). The pattern reflects well the expected six-fold symmetry of graphitic structures. However, three sets of spots are seen. This can be assigned to rotational stacking faults in the graphene layers, possibly derived from the process of intercalation and subsequent expansion.
Overall, the above analysis demonstrates that the TEG flakes were several tens of micrometers in lateral size with thicknesses beyond the tens of nanometers. Thus, they should be considered as microparticles of graphite. Interestingly, the crystallinity of the parent graphite intercalated compound is retained, this despite the rapid high-temperature expansion process.

### 4.2 Chemical exfoliation of TEG

The TEG was used as the initial material to investigate different approaches that could further exfoliate the flakes. These are divided below according to various parameters employed: solvent, an intercalating agent, ultrasonication and/or homogenizer.

#### 4.2.1 Solvent-guided exfoliation using ultrasonication

Details of the experimental procedure were explained in Chapter Two. Here, DMF was used as the dispersing solvent (at room temperature) for the ultrasonication procedure.
The first characterization step was to measure the lateral size distribution of the flakes. Given the smaller mass of product available (in relation to the initial TEG), the DLS set-up was used instead of the Master-Sizer tool (which commonly requires 50 mg or more of material). In Figure 4.8, a DLS plot is shown (the dispersing agent for the powder was ethylene glycol). Interestingly, the profile of size distribution is quite regular and places the flakes’ lateral dimensions within the interval of 0.7-1.3 µm. This is considerably different from the original TEG (cf. Figure 4.2). Still, it should be stressed that the analysis was carried out using different instrumentation.

![DLS plot](image)

**Figure 4.8:** Size distribution of TEG flakes exfoliated by boiling and ultrasonicating in DMF.

To understand the morphology of flakes with such reduced dimensions, SEM was performed on this sample. Figure 4.9 shows several examples of the exfoliated microparticles dispersed onto a silicon wafer. The flakes retained the jagged edges and overall graphite-like appearance previously showed by the TEG. It is also apparent that they are multi-layered and crumpled. While the imaged particles were smaller than those of the initial TEG, the average lateral size was larger (3-5 µm in
the SEM) than what the DLS identified. The lack of agreement in the sizes measured by DLS and SEM may be explained with limitations of the first technique in identifying larger particles.

**Figure 4.9:** SEM images of some TEG flakes exfoliated by boiling and ultrasoni- 
cating in DMF.

Further to imaging, the chemical composition was examined with EDS. The boxed region of the flake in **Figure 4.10 (a)** gave rise to signals of C, O and Si. Possibly due to the minor size and less corrugated shape of the flake (in relation to the initial TEG), the peaks from the SiO₂ substrate were also identified, as shown in **Figure 4.10 (b)**.
**Figure 4.10:** (a) Exfoliated flake prepared by boiling and ultrasonicing in DMF; (b) EDS spectrum of the region boxed in (a).

The results obtained for the height profile and AFM imaging of this sample are shown in **Figure 4.11**. The images and corresponding profiles show that the flakes have different lateral sizes ranging from ~100 nm to a few micrometers (<5 μm). For the major part, the thickness varied from 1 nm to 3 nm (e.g. **Figures 4.11 (a) and (b)**). These values are concurrent with the expected thickness of single- or few-layer graphene (as deposited on a SiO₂ substrate) [63, 64]. In addition to the smaller particles, thicker ones were also observed. In **Figure 4.11 (c)** one example of these is shown (thickness ~30 nm).
Figure 4.11: AFM images and respective height profiles of flakes prepared by boiling and ultrasonicating in DMF.
Figure 4.12 shows a Raman map and spectrum of one flake. The map was composed from the G and 2D band over an area of 100 µm x 50 µm. It is possible to see brighter regions which correspond to the smaller flakes described in the AFM analysis. The particle circled in (a) has a spectrum where two peaks are visible, corresponding to the G (1573 cm$^{-1}$) and 2D (2708 cm$^{-1}$) bands. The signal-to-noise ratio is low due to the thin nature of the flake added to the low acquisition time during the mapping procedure. While not entirely reliable, it is interesting to note that the I$_{2D}$/I$_{G}$ = 0.8, which gives further indication that these particles are less than 10 layers across. Similar results were reported in ref [65].

Figure 4.12: (a) Raman map of boiled and ultrasonicated TEG flakes dispersed in DMF onto a SiO$_2$ wafer; (b) Spectrum of an individual particle.

With the exception of the SEM results, the characterization of this sample (DLS, AFM and Raman) points to the presence of a high concentration of very thin graphene flakes. The process of sample
preparation for SEM analysis or, eventually, differences in contrast between the thicker and thinner carbon particles may have prevented the observation of the smaller flakes, explaining the mismatch. Overall, the TEG particles exfoliated by means of boiling and ultrasonicating in DMF had lateral sizes of a few micrometers and were less than 5 nm across. This represents a clear departure from the initial TEG particles described above.

4.2.2 Solvent-guided exfoliation using a homogenizer

The procedure followed was similar to that described in the previous section with the exception that a homogenizer was employed in place of the ultrasonic processor.

The particle size analysis was attempted with different set-ups. However, for one of these there was not enough product (MasterSizer) whereas for the other (DLS) no peaks were identified (this has to do with the larger size of the particles in this sample, i.e. beyond the measuring capabilities of the DLS – see below).

The morphology of flakes was studied with SEM as shown in Figure 4.13. The particles observed are <10 µm in lateral size with well-defined edges and crumpled/folded. In this respect, they portray micron-sized graphitic particles. The images are similar to those seen in Figure 4.9. This implies that both the ultrasonic processor and the homogenizer would not destroy the graphitic lattice by turning it into amorphous carbon, for instance.
Figure 4.13: Various flakes boiled in DMF and exfoliated (at room temperature) with a homogenizer.

Besides imaging, the chemical composition of these particles was examined with EDS (Figure 4.14). Once again, the elements identified were C, O and Si.

Figure 4.14: (a) Flake produced with assistance of the homogenizer, in DMF; (b) EDS spectrum of the area boxed in (a).

Figure 4.15 shows the AFM topography image and height profile of an individual particle. The lateral size of this flake was ~6 μm and the thickness at its edge was ~40 nm. The flake presents
folds of the graphene layers that point out-of-plane making its height hundreds of nm in these locations (very bright areas in the AFM image).

![AFM image of an isolated flake prepared by the homogenizer approach.](image)

**Figure 4.15:** AFM image of an isolated flake prepared by the homogenizer approach.

The optical microscopy and Raman spectroscopy for this sample is shown in **Figure 4.16**. Again, the spectrum of the isolated particle is characteristic of a graphitic material and the three expected bands, D, G and 2D, are observed. The frequency of the G band remains virtually unchanged relative to that of the original TEG material. The \( \frac{I_{2D}}{I_G} \) intensity ratio was around 0.45 with the 2D band being fairly asymmetric but of higher relative intensity when compared to that of the TEG. Interestingly, there was also a noticeable change in the D band. In fact, this particular flake seems to have a lower density of defects (\( \frac{I_D}{I_G} = 0.02 \)) than the previous samples. More details are provided in **Table 2**.
Figure 4.16: (a) Raman optical image of a flake exfoliated in DMF with a homogenizer and deposited on a SiO$_2$/Si wafer; (b) Raman spectrum of the particles in (a) with the outset showing the peak fit analysis for the 2D band.

Table 2: The Raman spectral frequency, FWHM and relative intensity, for the flakes prepared using the homogenizer.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1338</td>
<td>43</td>
<td>3%</td>
</tr>
<tr>
<td>$G$</td>
<td>1577</td>
<td>23</td>
<td>100%</td>
</tr>
<tr>
<td>2D (deconvoluted)</td>
<td>2719</td>
<td>30</td>
<td>45%</td>
</tr>
<tr>
<td></td>
<td>2698</td>
<td>89</td>
<td>45%</td>
</tr>
</tbody>
</table>

While it was not possible to assert the average lateral size from the particle analyzers, the optical, SEM and AFM analyses showed concurrent results in that the flakes were less than 10 µm in size. However, the minimum size of these was considerably larger than those sonicated in DMF (described above). As for their structure, the graphitic ordering is retained as identified by the low
intensity of the D-band. In regards to the thickness of the flakes, these appear to the thinner than the initial TEG, as per the AFM (40 nm) and I2D/Ig Raman results. Overall, the flakes obtained were smaller and thinner than the initial TEG ones.

4.2.3 Solvent-guided exfoliation using ultrasonication and an intercalant

After the work done with the boiling solvent followed by the ultrasonic processor and homogenizer in DMF, the next step was to introduce an additional exfoliation promoter, the intercalant Na2SO4 [66]. According to the literature, chemical expansion provides a further choice for scalable, high-yield graphene production. Current studies have revealed that some intercalation molecules (e.g. Na2SO4) can be used to produce expanded graphite with electrochemically-induced exfoliation [67]. The first experiment was therefore to combine the chemical/mechanical action of the ultrasounds with the solvent and intercalant.

As previously, there was not enough product to undertake a satisfactory particle analysis. Likewise, DLS did not identify peaks for <2 µm.

The SEM analysis of the flakes is shown in Figure 4.17. The majority of these had a lateral size of <10 µm. Once again, they showed folds and were constituted by staked layers of graphene in different orientations.
Figure 4.17: Typical SEM images of flakes prepared by intercalating Na$_2$SO$_4$ in boiling DMF followed by ultrasonication.

In addition to imaging, the chemical composition was examined with EDS. In Figure 4.18 (a), a small and isolated flake is imaged. The spectrum in Figure 4.18 (b) identifies the presence of C, O and Si. The main signal is Si, which is generated from the SiO$_2$ substrate. Since the electron beam can penetrate deeply through the thin particle, the Si substrate peak is dominant over C.

Figure 4.18: (a) Isolated flake; (b) EDS spectra for the region marked in (a).
The AFM study of a discrete flake is presented in Figure 4.19. The flake’s lateral size is about 6 \( \mu \)m and shows areas considerably thinner than others. The height profile taken at the edge of the particle gives a thickness of 4 nm. Logically, this is larger in the middle of the flake due to folds, etc. and from there, the height scale could reach a value of up to 200 nm.

**Figure 4.19:** (a) AFM images of a flake prepared by intercalating Na\(_2\)SO\(_4\) in DMF; (b) Corresponding height profile.

In Figure 4.20 (a), two particles were imaged with the optical microscope. The smaller of these was studied. After acquiring the Raman spectrum (Figures 4.20 (b-c)), the intensity ratio I\(_D\)/I\(_G\) obtained is 0.2 whereas the I\(_{2D}\)/I\(_G\) is 0.1. The 2D peak was identified as arising from multilayer graphene. In all of these Raman spectra, the presence of folding makes the task of interpreting its thickness much more challenging. As for the structure, the low D-band confirms the high structural order of the material. More details are given in Table 3.
Figure 4.20: (a) Optical image of two flakes deposited on SiO$_2$/Si wafer; (b) Raman spectra of the smaller particle boxed in (a) with the respective 2D peak fit shown in the outset (c).

Table 3: The Raman spectral frequency, FWHM and relative intensity of a flake prepared by intercalating Na$_2$SO$_4$ in boiling DMF solvent and followed by ultrasonication.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1344</td>
<td>49</td>
<td>2%</td>
</tr>
<tr>
<td>$G$</td>
<td>1573</td>
<td>23</td>
<td>100%</td>
</tr>
<tr>
<td>2D (deconvoluted)</td>
<td>2668</td>
<td>128</td>
<td>21%</td>
</tr>
<tr>
<td></td>
<td>2700</td>
<td>63</td>
<td>21%</td>
</tr>
</tbody>
</table>
4.2.4 Solvent-guided exfoliation using a homogenizer and an intercalant

In this second set of experiments with the intercalant (Na$_2$SO$_4$), the homogenizer was used in place of the ultrasonic processor. As previously, there was not enough product to undertake a satisfactory particle analysis in solution.

Concerning the SEM characterization, typical images of the homogenized flakes are shown in Figure 4.21. The flakes were clearly graphitic, thin and had lateral sizes of <10 µm. Generally, their morphology did not deviate much from the previous examples.

![Figure 4.21: Typical SEM images of the flakes exfoliated in boiling DMF with intercalant and using a homogenizer.](image)

The chemical composition, taken from the flake in Figure 4.22 (a), identified C, O and Si. Possibly due to the minor size and less corrugated shape of the flake, the peaks from the SiO$_2$ substrate were dominant in the EDS spectrum (Figure 4.22 (b)).
As for the AFM study, the height profile and topography images of this sample are shown in Figure 4.23. The two selected flakes are similar to previous examples apart from the large flat area that dominates the flake in Figure 4.23 (a). This smooth surface is confirmed by the regularity of the height profile in Figure 4.23 (d). The thickness of these particles varied from 40 nm to 100 nm.
Figure 4.23: (a-b) AFM images of two typical flakes prepared by intercalating Na$_2$SO$_4$ with boiling DMF followed by homogenizer exfoliation and deposited onto a SiO$_2$/Si wafer and the corresponding thickness measurements.

The Raman spectra of several flakes were collected. The first example of these is shown in the optical image of Figure 4.24 (a). The signal-to-noise ratio of the corresponding spectrum in Figure 4.22 (b) was significantly low, visible from the D band which was almost hidden by the background noise. The frequencies and other aspects of the main bands are given in Table 4. After the baseline correction, the I$_D$/I$_G$ was 0.29 and the I$_{2D}$/I$_G$ was 0.5. Figure 4.24 (c) shows that 2D peak results from a conjunction of overlapping peaks which signals the presence of multilayer graphene.
**Figure 4.24:** (a) Optical image of an isolated particle; (b) Raman spectrum of the flake in (a); (c) Peak fitting for the 2D band in (b).

**Table 4:** The Raman spectral frequency, FWHM and relative intensity of a flake prepared with intercalant Na2SO4 followed by homogenizer processing.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency $(cm^{-1})$</th>
<th>FWHM $(cm^{-1})$</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1344</td>
<td>41</td>
<td>10%</td>
</tr>
<tr>
<td>$G$</td>
<td>1577</td>
<td>24</td>
<td>100%</td>
</tr>
<tr>
<td>2D</td>
<td>2711, (deconvoluted)</td>
<td>41, 172</td>
<td>45%, 45%</td>
</tr>
<tr>
<td></td>
<td>2693</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

A second example that was studied is given in **Figure 4.25 (a)**. This flake is smaller but its spectrum is similar to one in **Figure 4.24**, again with the signal-to-noise ratio being very low. The D, G and 2D bands were identified at 1344 cm$^{-1}$, 1575 cm$^{-1}$ and 2720 cm$^{-1}$, respectively.
The analysis of the samples obtained from ultrasonication and homogenizer processing showed that similar products were obtained. Overall, the particle size was a few micrometers in lateral size and thickness was up to 100 nm.

### 4.2.5 Size-fractioned TEG

Following the work described above, where different exfoliation strategies for TEG were explored, a second set of experiments was developed. This attempted to obtain a smaller size distribution for the flakes as opposed to the initial TEG material. The experimental procedure followed to obtain the size-fractioned product is explained in Chapter Two.

In regards to the characterization, the first step was to study the size distribution of the particles in solution (with a particle size analyzer). The amount of product obtained using the 60 μm filter was in enough quantity to work with the MetaSizer. The analysis of the curve in **Figure 4.26** shows an...
asymmetrical unimodal distribution with a mode peak at 18 µm. The percentile 50% is at 20 µm while the 80% level is at 31 µm. Overall, it can be stated that the majority of the particles lie in the interval of 15-30 µm.

Figure 4.26: Size distribution of the size-fractioned TEG as dispersed in water, at room temperature.

Besides this initial experiment, further tests were performed to show both the effect of precipitation/filtration and rotation speed during the operation of the particle size analyzer. Figure 4.27 shows various size distribution plots of the TEG. These had similar obscuration value (3-5%), i.e. the dispersion concentration was comparable. During the operation of the analyzer, the rotation speed was kept constant at 2500 rpm. In the first approach, when simple solvent agitation was used and the particles were left to deposit naturally, a broad size distribution was found (Figure 4.27 (a)). On the second approach, when a 20 µm net filter was used, a narrower size distribution was obtained, see Figure 4.27 (b). These results imply that while the mode size may be similar the use of a filter membrane leads to a narrower size distribution. Still, there were instrumental factors in
the analysis with the MasterSizer that were addressed to confirm the size distribution. Hence, it is interesting that when the blade speed was reduced to 1500 rpm (Figure 4.27 (c)), the size distribution was effectively narrowed. This rotation speed was found to be optimal for the obscuration interval of 3-5% when analyzing TEG flakes.

![Figure 4.27: Size distribution plots for TEG flakes. (a) After using the solvent agitation technique (at 2500 rpm); (b) After fractionation through a 20 µm net filter (at 2500 rpm); (c) After fractionation through a 20 µm net filter (at optimal 1500 rpm).](image)

While the 1500 rpm was optimal, the plot still showed a tail (Figure 4.27 (c)). This is common to all plots and while it was reduced at 1500 rpm, it represents an instrument artefact. To clarify the 1500 rpm result in a more significant way, a Gaussian curve fitting was performed (Figure 4.28). With this, it was observed that the mean size of the filtered TEG was ~18 µm and the FWHM was 15 µm.
The single-particle morphological and size analysis was carried out with SEM imaging. Figure 4.29 shows a set of representative examples of filter-fractioned TEG particles. The low-magnification analysis (Figures 4.29 (a) and (b)) clearly shows a sample where the majority of the particles have similar sizes. This size uniformity was not seen for any of the previous products and can be assigned to the fractioning procedure using the filter. Generally, the flakes observed (in dry-state) ranged from 1 \( \mu \text{m} \) to 15 \( \mu \text{m} \). From the extensive analysis, it was concluded that ~90% of the deposited particles were 10-15 \( \mu \text{m} \) (Figures 4.29 (c–f)).
Figure 4.29: Typical SEM images of TEG flakes after size-fractionation with 20 µm filter.

Given the size uniformity seen with the SEM, the internal structure of the flakes was studied with TEM. Examples of the multilayered particles can be seen in the low-resolution TEM images (Figure 4.30 (a-d)). To determine the exact thickness of the individual flakes, high-resolution imaging was performed. For this, the electron beam and the graphene planes have to become parallel, i.e., at the folding edge where the planes diffract electrons, and these are seen as dark lines in the phase contrast image (Figure 4.30 (e)). Simply, one line thickness is equivalent to the thickness of one graphene sheet. In this respect, the flakes were about 20 layers (corresponding to 70 nm) that were well-aligned, corroborating the view of retention of the graphitic lattice.
Figure 4.30: Typical TEM images of the TEG flakes after size fractionation. (a-b) Low-resolution TEM images (the inset shows the respective ED pattern); (c-d) Medium resolution TEM images of additional TEG flakes; (e) High-resolution TEM image of the folding edge of a flake.

The high-resolution imaging was followed by the single-particle diffraction analysis in reciprocal space. **Figure 4.30 (a, inset)** above shows the typical electron pattern of these flakes. The pattern shows the six-fold symmetry of several superimposed graphitic grains with orientation variations. It is possible to identify between 5 and 7 sets of hexagonal spots.

The size-fractioned sample was then studied with AFM. **Figures 4.31 (a) and (b)** show the topography of two selected flakes and respective height profiles. While the lateral size of these and similar flakes (<15 μm) was well within the range already described from the particle analyzer, SEM, and TEM, the thickness measured was normally between 70 and 200 nm. The lower limit agrees well with the HR-TEM results given above.
Figure 4.31: AFM images and respective height profiles of the size-fractioned TEG flakes.

Figure 4.32 presents the results of the Raman spectroscopy analysis of this sample. Figure 4.32 (a) shows an image from a fractioned flake obtained using optical microscopy. Next, the corresponding spectrum is shown in Figure 4.32 (b) and the fit of the 2D is given in Figure 4.32 (c). The peak for the G band was at \( \sim 1575 \text{cm}^{-1} \). This value corresponds to the \( E_{2g} \) mode of graphite which is related to the vibration of the sp\(^2\) carbon atoms that are bonded in a two-dimensional hexagonal lattice. For the D-band, the small peak was at \( \sim 1344 \text{ cm}^{-1} \). This peak shows the low disorders and the defects present in the hexagonal layer. For the 2D band, the peak was at \( \sim 2715 \text{ cm}^{-1} \) as shown in Figure 4.32 (b). Interestingly, the value of \( I_D/I_G \) was reduced from the case of the initial TEG. This change
can be attributed to the structural defects leading to boundary edges increase for the graphene flakes. **Figure 4.32 (c)** shows the deconvolution of the 2D band was carried out to show its lack of symmetry.

![Figure 4.32](image)

**Figure 4.32** (a) Optical microscopy image of a fractioned TEG flake; (b) Raman spectrum of the flake in (a); (c) Peak fitting of 2D band; (d-f) Spectroscopic Raman mapping of the flake in (a) with normalized intensity maps of the D, G and 2D bands, respectively.
Next, the 2D maps for the flake were composed from the Raman spectrum using energy filters. **Figures 4.32 (d-f)** show the maps for the D, G and 2D bands, respectively. In **Table 5** more details of the Raman spectral data are provided.

**Table 5**: The Raman spectral data for frequency, FWHM and relative intensity of the main bands of TEG flakes after size-fractionation.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm(^{-1}))</th>
<th>FWHM (cm(^{-1}))</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>D</td>
<td>1350</td>
<td>187</td>
<td>5%</td>
</tr>
<tr>
<td>G</td>
<td>1574</td>
<td>22</td>
<td>100%</td>
</tr>
<tr>
<td>2D</td>
<td>2713 (deconvoluted)</td>
<td>28</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>2689</td>
<td>71</td>
<td>25%</td>
</tr>
<tr>
<td></td>
<td>2677</td>
<td>171</td>
<td>25%</td>
</tr>
</tbody>
</table>

A second flake was analyzed and the optical microscopy image is given in **Figure 4.33 (a)**. From **Figure 4.33 (b)**, a very small D band with a value of \(\sim 1344\) cm\(^{-1}\) was identified. The G band appeared at \(\sim 1575\) cm\(^{-1}\). The 2D peak was observed at 2703 cm\(^{-1}\) which may be assigned to the presence of multilayer graphene flakes. The lack of symmetry in the 2D band was observed and a deconvolution of it done, **Figure 4.33 (c)**. Further information is given in **Table 6**. After applying a baseline correction, the values for \(I_D/I_G\) and \(I_{2D}/I_G\) were 0.07 and 0.35, respectively. **Figures 4.33 (d-f)** show the Raman mapping for the spectra collected.
Figure 4.3: (a) Optical microscopy image of a TEG flake; (b) Raman spectrum of the flake in (a); (c) Peak fitting of 2D band; (d-f) Spectroscopic Raman mapping of the flake in (a) with normalized intensity maps of the D, G and 2D bands, respectively.

Table 6: The Raman spectral data of frequency, FWHM and relative intensity for the flake in Figure 4.33.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1401</td>
<td>624</td>
<td>7%</td>
</tr>
<tr>
<td>$G$</td>
<td>1575</td>
<td>25</td>
<td>100%</td>
</tr>
</tbody>
</table>
The set of characterization tools used allowed to make some general conclusions for this sample. Overall, the size of the flakes was 10-20 μm while the thickness was between 70 to 100 nm. The fractioning procedure developed was clearly successful, as the main objective of this experiment was to reduce the lateral size distribution. Note that, as described above, the initial TEG had flakes that were mostly in the interval 20-70 μm while the thickness was between 60 to 100 nm. It is also important to stress that the fractioning process did not induce structural damage on the particles. In fact, when compared to the initial TEG flakes the value for $I_D/I_G$ was reduced. This could be related to the decrease in the boundary edges and crumples.

### 4.2.6 Exfoliation of the size-fractionated TEG

A wide distribution of particle sizes leads to an added variable in the process of exfoliating graphitic flakes as it becomes reasonable to question “how does the lateral particle size affect the efficiency of the exfoliation process?”. Following the size-fractionation process, the lateral size of the flakes was more uniform, so it was possible to re-access the exfoliation approach and see if some of the results were different. The method for exfoliation used was boiling in DMF with intercalant followed by ultrasonication.

Given that the amount of product obtained was not enough to analyze the particles size with dispersions, the SEM was used (Figure 4.34). The low magnification image in Figure 4.34 (a) gives an overall view of the samples as it was dispersed on the patterned substrate (this was
necessary to localize these smaller sized particles sample). The individual flakes presented in

**Figures 4.34 (b-f)** illustrate that the exfoliated-fractioned particles were <10 µm in lateral size but retained its folded nature.

![SEM images](image)

**Figure 4.34**: SEM images for fractionated flakes prepared by intercalating Na$_2$SO$_4$ in boiling DMF followed by ultrasonication.

In order to ensure that the intercalant did not remain inside the flakes, EDS was used to confirm the chemical composition (**Figure 4.35**). Three elements were identified C, O and Si. Probably due to the minor size and less corrugated shape of the flake, the peaks from the SiO$_2$ substrate were dominant.
The AFM assessment was performed to determine the thickness of the fractionated TEG layers after exfoliating them. In Figure 4.36, the topographic height of the particle edge layers is 40 nm and the lateral dimension at this location is about 0.8 μm. The entire flake is almost 4 μm in its longest axis.

Figure 4.35: (a) Representative exfoliated-fractioned TEG flake; (b) EDS spectrum of the region marked in (a).

Figure 4.36: (a) AFM topography image of a discrete flake; (b) Height profile of the flake in (a).
**Figure 4.37** shows the optical image and Raman spectrum of a typical TEG flake, after fractioning and exfoliation. The D and G bands appear at ~1354 cm$^{-1}$ and 1583 cm$^{-1}$, respectively. In **Figure 4.24 (c)** the results of the 2D peak deconvolution are given (~2713 cm$^{-1}$). Again, the band shows the typical signal arising from multilayer graphene particles. The intensity ratio I$_{D}$/I$_{G}$ obtained after a baseline correction is 0.08 and I$_{2D}$/I$_{G}$ was 0.37 (**Table 7**).

**Figure 4.37:** (a) Optical image of a selected flake; (b) Raman spectra of exfoliated-fractioned TEG flake and (c) the peak fit of the 2D band.

**Table 7:** The Raman spectral data of frequency, FWHM, and relative intensity for the fractionated flakes prepared by intercalating Na$_2$SO$_4$ followed by ultrasonication.

<table>
<thead>
<tr>
<th>Band</th>
<th>Frequency (cm$^{-1}$)</th>
<th>FWHM (cm$^{-1}$)</th>
<th>Relative intensity</th>
</tr>
</thead>
<tbody>
<tr>
<td>$D$</td>
<td>1346</td>
<td>31</td>
<td>3%</td>
</tr>
<tr>
<td>$G$</td>
<td>1582</td>
<td>24</td>
<td>100%</td>
</tr>
</tbody>
</table>
The above product was further characterized with TEM. One flake is shown in the low resolution of Figure 4.38 (a). Inset, the electron diffraction pattern shows the typical six-fold symmetry diffraction ring which is associated with graphitic materials [68]. High-resolution TEM imaging was performed to assert the thickness of these flakes. Several were examined. In Figures 4.38 (b-d), the flakes probed look very thin. It was possible to identify edges of the flakes were bilayer, trilayer and few-layers were observed. Some of these particles also had small lateral size (about 1 μm).
Figure 4.38: Typical TEM images of exfoliated-fractionated TEG flakes. (a) Low resolution image of an isolated flake with electron diffraction pattern, inset; (b-d) High-resolution images showing that the flakes had regions that were considerably thin, just a few layers thick.

In this exfoliated-fractioned sample, the flakes were mostly <10 µm of lateral size and thickness of 40 nm. Overall, the process did not result in particles that were much thinner than the fractioned TEG. Remarkably, the TEM showed flakes where very thin edge sections exist, sometimes bearing only two layers.
Chapter 5 – Final Discussion

A commercial graphite intercalated compound (GIC) was thermally expanded and processed to yield the starting product for this thesis work, thermally-expanded graphite (TEG). These flakes were seen to retain the structural integrity of the carbon lattice in the parent GIC.

Several approaches to further exfoliate the TEG were then explored. In common, the use of boiling DMF. Preliminary experiments showed this solvent to be the most efficient in dispersing and exfoliating the TEG powder. The high temperature here employed was something that had not been tested in the literature before and assumed to aid in the dispersion as well as accelerate the rate of exfoliation. Further to the boiling solvent, a second step was introduced wherein shear forces were applied to the DMF dispersion (at room temperature) either by the action of a homogenizer or an ultrasonic processor. When using ultrasonication, different populations of flakes were obtained. Some of the particles had lateral sizes of a few µm and thickness of around 30 nm, whereas others were seen to be as small as 100 nm and 1 to 3 nm thick. Raman analysis was consistent with this interpretation through the $I_{2D}/I_G$ ratio that pointed to the presence of few-layer graphene. The use of the homogenizer was not as successful as it resulted in flakes that were larger; in average, with <10 µm in lateral size and thickness of ~40 nm.

The introduction of an additional exfoliation promoter was done in view of reports that asserted the efficient of the intercalant Na$_2$SO$_4$ for this purpose. By adding the salt to the boiling DMF solution, the initial TEG powder should be further exfoliated. This hypothesis was not seen to be correct as, irrespective of using ultrasonication or the homogenizer, the resulting flakes were about
<10 \mu m \text{ with a thickness of up to } 200 \text{ nm (possibly due to folding). This did not however impair the observation of sections of random flakes where indeed small cross-sections were measured.}

Following this, and because the size of the initial TEG flakes was not uniform, a size-fractioning method was developed. Several approaches were attempted such as agitation followed by precipitation or the use of track-etched filtering membranes. The second method revealed to be particularly efficient. The size distribution of the flakes obtained was consistently seen to be in the interval of 10-20 \mu m with a mean peak at 18 \mu m. The heights had ranged from 70 to 200 nm. The product of this fractioning process was further subjected to one of the processes previously carried out, namely the one using an intercalant in conjunction with the boiling solvent followed by ultrasonication. The question was whether having uniform-sized particles would result in a better exfoliation yield. The resulting flakes were still some \mu m in size and tens of nm thick. However, it was possible to identify sections of the flakes that were considerably thinner (4-10 nm). It is possible that longer exposure to boiling solvent and intercalant could have led to a more efficient exfoliation.

Overall, the best results were obtained from boiling the TEG flakes in DMF and following this with the ultrasonication process. With this, it was possible to obtain particles that were in the sub-micron lateral size range and consisted of only a few stacked graphene layers. Also, it was shown that membrane filters can efficiently reduce the size distribution of the particles and define the mean size of these (via the size of the filter pores).
Chapter 6 – Conclusions and Outlook

To facilitate the translation of graphene from the lab to industry and commercial applications, it is necessary to develop simple and cost-effective methods to produce high-quality FLG. The body of literature is coherent in its view that top-down approaches, particularly those based on liquid-phase intercalation/exfoliation, are the most practicable. Many issues persist to develop a truly satisfactory production process where shape, lateral size and thickness of the flakes are controlled on-demand.

In this thesis, the use of a high-temperature exfoliating organic solvent and an intercalant salt was explored along with shear mixing, using either an ultrasonic processor or a homogenizer. To control the lateral size of the flakes, a size-fractioning procedure was tested. Overall, it was found that boiling thermally-expanded graphite (TEG) in DMF and following this with an ultrasonication step done at room temperature generated the smallest and thinnest FLG flakes. However, this product was not homogeneous as the initial TEG particles varied greatly in size. Testing of a filter-membrane procedure for size-fractioning showed that it was possible to address the size-dispersion issue. However, reducing the flakes nominal size does not necessarily result in more efficient exfoliation. This implies that an exfoliation procedure that does not work on the initial TEG particles will also not work on the size-fractioned ones.

Due to time constraints, it was not possible to test the size-fractioned TEG with the best exfoliation procedure reported, i.e. boiling DMF followed by ultrasonication. Future work should therefore address this question and consider whether the size-fractioning and exfoliation in DMF can be scaled up to handle hundreds of mg (or even grams) of the TEG material.
References


