Modelling the exfoliation of graphite for production of graphene

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Department of Engineering Sciences
Abstract

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The aim of my thesis is to make a theoretical model of data obtained from liquid-phase exfoliation of graphene. The production of graphene in the liquid phase exfoliation is a cost efficient method. One part of this work is devoted to learn the method of production of graphene by the shear mixing technique from the graphite and to estimate some important parameters which are crucial for the process.

Other part of my work is based on studying the liquid-phase exfoliation mechanism of graphene through ultra-sonication technique. This method is time consuming as compared to shear-mixing.
Acknowledgements

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Mehwish Abro,

Uppsala University, Sweden

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Introduction

Graphene, \(^1\text{-}^3\) is a two dimensional nanomaterial consist of single atomic layer of sp2-bonded carbon atoms. \(^4,5\) It is organized in a honeycomb lattice/ benzene like structure, displays amazing electronic, electrical, mechanical, optical and thermal properties.\(^6,7,8\) In the most recent decade graphene has developed as an energizing new material, with potential to affect numerous areas of science and innovation.\(^9,10\) With an innovative method (Scotch-Tape exfoliation) Novoselov and Geim in 2004 have successfully exfoliated monolayers of graphene and awarded the Nobel prize in Physics.\(^11,12\) It is semimetal material having several outstanding applications. According to the properties for example, electronic devices as micro- and optoelectronics\(^13,14,15,16,17\), basic nanocomposites, printed electronics, conductive coating, biological labeling \(^18\) and batteries and supercapacitors.\(^19\) Many other possible technological applications of monolayer graphene, e.g. in photonics and flexible electronics, ranging from solar cells\(^20\), photodetector\(^21,22,23\) and light emitting devices\(^24\) to touch screens\(^25\), ultrafast lasers\(^26\), spin valves\(^27,28\) etc., are additionally being investigated.

Structure

Graphite was derived from the Greek word ‘Graphein’ which means to write. The term graphene was derived from the graphite, presented by chemists Hanns-Peter Boehm and co-worker in 1986.\(^29,30\) Graphite is the combination of the millions of the graphene layers. Two types of bond are formed among the graphene layers. The bond which holds together the layers of graphene by the weak force called Vander Waal attraction. The Vander Waal bond length between the adjacent graphene layers is 3.41Å (0.341nm).\(^3\) Due of this weak attraction between layers, the layers slide each other and the attraction is strong enough to do the complete exfoliation into individual layers. Another bond known as Covalent bond which present between the carbon-carbon atoms in each layer is 1.42Å (0.142nm) considered as the strong bond.\(^31\) Both the hypothetical and experimental research proved that the properties of graphene are mainly dependent on their geometric structures. (See Figure 1)

![Graphene structure](https://www.google.se/search?q=graphene+structure&espv=2&biw=1920&bih=935&source=lnms&tbm=isch&sa=X&ved=0CAYQ_AUoAWoVChMI1KXMptTiyAIvPjdyCh11AArw#imgrc=xMbdpfJEXG22SM%3A)
Properties of Graphene

Graphene has many outstanding properties. It is considered as the thinnest possible material in the world and compared to the steel it is 200 times stronger material.\textsuperscript{32,33} According to Hoornad and their colleagues the thermal conductivity of graphene is ~33 times greater than the silicon.\textsuperscript{34} Below given are the important properties of graphene which are collected from different literature.

<table>
<thead>
<tr>
<th>Sr.</th>
<th>Property</th>
<th>Value</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.</td>
<td>Large Surface Area</td>
<td>$\sim (3000 \text{ m}^2\text{g}^{-1})$</td>
<td>30,36</td>
</tr>
<tr>
<td>2.</td>
<td>Stretch elasticity</td>
<td>$\sim 20%$</td>
<td>51</td>
</tr>
<tr>
<td>3.</td>
<td>Optical Transparency</td>
<td>$\sim 97.7%$</td>
<td>37,38</td>
</tr>
<tr>
<td>4.</td>
<td>Tensile Strength</td>
<td>$\sim (130\text{GPa})$</td>
<td>30,39</td>
</tr>
<tr>
<td>5.</td>
<td>Thermal Conductivity</td>
<td>$\sim (3000-5000)\text{WmK}^{-1}$</td>
<td>30,40,41,42</td>
</tr>
<tr>
<td>6.</td>
<td>Breaking Strength</td>
<td>$\sim (42\text{Nm}^{-1})$</td>
<td>10,40</td>
</tr>
<tr>
<td>7.</td>
<td>High Carrier Mobility</td>
<td>$\sim (10,000\text{cm}^2\text{V}^{-1}\text{S}^{-1})$</td>
<td>36,39,41,39,42,48</td>
</tr>
<tr>
<td>8.</td>
<td>Young’s Modulus</td>
<td>$\sim (1.0\text{TPa})$</td>
<td>30,39,41,41</td>
</tr>
<tr>
<td>9.</td>
<td>Large Spring Constant</td>
<td>$\sim (1-5\text{Nm}^{-1})$</td>
<td>30,39,49</td>
</tr>
<tr>
<td>10.</td>
<td>Electrical Conductivity</td>
<td>$\sim (3000 \text{Wm}^{-1}\text{k}^{-1})$</td>
<td>50</td>
</tr>
</tbody>
</table>
Common Methods for Graphene synthesis
There are tremendous efforts have been done to develop synthesis methods for graphene. These different methods are used to achieve high yield of graphene for different application. Generally the synthesis methods can be classified as the Top-Down and Bottom-Up approaches. All the methods have their own pros and cons depend on final applications. Many researchers proved that the graphene production by bottom-up methods have high quality but unfortunately suffers from low scalability. On the other hand the graphene produced by Top-down methods have high quantity but poor quality. The production of graphene in the large scale and at low cost as explained by the top-down techniques. Precise control over graphene synthesis is therefore required for testing their fundamental physical properties and then introduce them in promising applications.

<table>
<thead>
<tr>
<th>Top-Down</th>
<th>Bottom-Up</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Mechanical Exfoliation</strong>&lt;sup&gt;4,42,53&lt;/sup&gt;</td>
<td><strong>Chemical Vapor Deposition (CVD)</strong>&lt;sup&gt;37,42,53,56,59,60&lt;/sup&gt;</td>
</tr>
<tr>
<td>(1) Apply the adhesive tape on graphite block and peeled back</td>
<td>(1) A substrate usually copper (sometimes Ni) is heated in furnace about ~1000°C at low pressure</td>
</tr>
<tr>
<td>(2) Join the two pieces of tape together to reduce layers</td>
<td>(2) CH&lt;sub&gt;4&lt;/sub&gt; and H&lt;sub&gt;2&lt;/sub&gt; gasses are added through furnace</td>
</tr>
<tr>
<td>(3) Finally press the tape on the smooth silicon substrate &amp; peel back leaving atomic single layer thick graphene.</td>
<td>(2) Seal the box in non-reactive environment and heated at about ~1500°C</td>
</tr>
<tr>
<td><strong>Liquid Phase Exfoliation</strong>&lt;sup&gt;53,54,55&lt;/sup&gt;</td>
<td><strong>Epitaxial Growth on Silicon Carbide 42,53,59,60</strong></td>
</tr>
<tr>
<td>(1) In this process ultrasound is used to break graphite into flakes into organic solvents.</td>
<td>(1) Small amount of SiC is placed into box with small hole in it</td>
</tr>
<tr>
<td>(2) After some duration, large quantity of flakes are produced</td>
<td>(2) Carbon atoms are deposited on copper substrate and continuous graphene sheets are formed.</td>
</tr>
<tr>
<td>(3) Centrifuge process is helpful for enriching the graphene quality.</td>
<td>(3) Because of heating, Si molecule from the surface of SiC evaporates, leaving high quality monolayer graphene.</td>
</tr>
</tbody>
</table>

**Chemical Exfoliation Via Graphene Oxide**<sup>56,57</sup>
(1) In this process the graphite is first oxidized and then exposed in chemical exfoliation to produce graphene oxide flakes
(2) Centrifuge process is used for further enriching of graphene sheets
(3) The solution is deposited on substrates and reduced thermally and chemically to get graphene.
## Common Methods Yield and their Applications

<table>
<thead>
<tr>
<th>Methods</th>
<th>flake size (Top view)</th>
<th>Cost</th>
<th>Throughput</th>
<th>Flake thickness (cross section view)</th>
<th>Number of layers</th>
<th>Applications</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mechanical process</td>
<td>Greater than 1 mm</td>
<td>low</td>
<td>low</td>
<td>10 nm</td>
<td>Single &amp; multiple</td>
<td>Research purpose</td>
</tr>
<tr>
<td>Chemical Exfoliation</td>
<td>1 μm</td>
<td>low</td>
<td>μm to few nm</td>
<td>μm to few nm</td>
<td>Single and multiple</td>
<td>Inkjet printer ink, polymers fillers, coating, paint, composites, transparent electrode, sensors, energy storage and bio applications</td>
</tr>
<tr>
<td>Chemical Exfoliation Via Graphene Oxide</td>
<td>μm to few nm</td>
<td>low</td>
<td>high</td>
<td>nm</td>
<td>Single and multiple</td>
<td>Inkjet printer ink, polymers fillers, energy storage, Battery electrodes, supercapacitors</td>
</tr>
<tr>
<td>CVD</td>
<td>cm</td>
<td>high</td>
<td>Moderate</td>
<td>&lt; 1 nm</td>
<td>Monolayer to multilayer</td>
<td>Touch screen, small windows, flexible LCDs &amp; LEDs</td>
</tr>
<tr>
<td>Epitaxial Growth on Silicon Carbide</td>
<td>100 mm</td>
<td>high</td>
<td>low</td>
<td>&lt; 1 nm</td>
<td>Monolayer to multilayer</td>
<td>Transistor circuits, interconnect, memory</td>
</tr>
</tbody>
</table>
**Liquid Phase Exfoliation:**
The exfoliation of graphite in the liquid environments can be effectively done by exploiting shear mixing and ultrasound to extract individual layers. The liquid phase exfoliation process normally includes three stages.(see figure: 2)

1. Dissolve graphite in a solvent,
2. Exfoliation, and
3. Purification.

![Shear Mixing Exfoliation](image)

![Ultra-sonication Exfoliation](image)

**Figure 2: Synthesis of graphene by two different methods in Liquid based exfoliation**

Liquid phase exfoliation is a method to exfoliate graphite into liquid solution. It is a feasible way to obtain colloidal suspension of graphene layers in the solution. The quality and quantity of graphene layers are higher than those produced from graphite oxide due to the absence of oxygen functionalities which disturb the properties like electrical conductivity and carrier mobility of graphene layers. This method is more efficient when the applied force to the graphene can overcome the graphene–graphene interlayer van der Waal interaction force. According to Loh et.al, the exfoliation is better when the surface energy of the solvent is close to the graphene. By the mechanical force, which is sufficiently greater than Vander Waals force, we can separate graphene layers.
The mechanical force is achieved by either sonication or shear-mixing. The long term sonication prompts to undesirable fragmentation into exfoliated graphene layers which brings about small size graphene layers. Generally, sonication is a process to transfer the sound energies to fragment the particles. It has been found that the surface energies play important role when graphite surface is immersed in the liquid. Liquid phase exfoliation is one of the effective and straightforward method to decrease the strength of the Vander Waals attractions.

Meanwhile in shear mixing and ultra-sonication, the growth and the breakdown of the micrometer-sized bubbles because of pressure fluctuations, work over the bulk material and induce exfoliation. After exfoliation, the interaction of solvent–graphene needs to adjust the attractive forces in between the inter-sheets. Ideal solvents to disperse graphene are those that actually minimize the interfacial surface tension \[\text{mN m}^{-1}\] between the solvent and graphene flakes. For example, the forces that reduce the area of the surfaces in contact.

Many groups have worked in this method and made it possible to produce large scale of graphene. Stankovich and their followers oxidized the graphite and produced the graphite oxide layer. During the oxidation process, the functional groups like hydroxyl and epoxide attached covalently to the graphite oxide reducing the interlayer interactions, which causes complete exfoliation and produce the single layer GO. The presence of oxygen functional group on the GO causes sheet hydrophilic and shows less thermal, electrical and mechanical properties as compared to pure graphene. So reduction of GO into graphene has become main area of research. Recently, some groups demonstrated the exfoliation of GO into the organic solvent like dimethyl foraminde (DMF), N-methyl-2-pyrrolidone (NMP), ethylene glycol and tetrahydrofuran (THF) with moderate sonication.

Hernandez and their fellows in 2008 explained the first successful exfoliation of graphite in the organic solvent such as NMP and DMF by sonication based technique. After centrifugation, they confirmed their characterization through Atomic Force Microscopy (AFM) and Transmission Electron Microscopy (TEM), that they obtained pristine graphene which were chemically unmodified. Surprisingly they achieved closely 100% graphene nanosheet and atomic thickness was less than 6 layers and samples was consisting of 28% monolayers. But NMP and DMF liquid have a few drawbacks e.g. NMP is an eye irritant and may be dangerous to the reproductive organs, while DMF may have toxic effects on various organs. It is considered that the solvents having the surface energy close to the graphene are appropriate for the direct exfoliation of graphene.

Mustafa Lotya et al in 2009 demonstrated that the mechanism of liquid phase production of graphene depends on utilizing the specific solvents whose surface energies are around that of graphene. These organic solvents require unique consideration when handling. However, it is considered that the solvents which have low boiling point is good for exfoliation of graphene but that graphene has limit application, while on the other hand the solvents which have high boiling point like (NMP 203 °C, cyclohexanone 156 °C and DMF 154 °C ) are suitable for the exfoliation of graphene but the high boiling points of these solvents restrict their use for the real manipulation, specifically in organic electronics. Many independent group explained unfortunately that water has a surface energy (72.7 mJm\(^{-2}\)) too much high to use it as for exfoliation of graphene.

In 2010 a group from Ireland which observed the dispersion of graphene in NMP solvent by using ultra sonication exfoliation method at low power 23W for long times up to 460hours. They have achieved
the concentration of 1mg mL\(^{-1}\). The size and thickness of flakes decrease with sonication time. For long sonication times the average flakes dimension still remains above 1μm. \(^{82}\)

The graphene application’s market is basically driven by progress in the synthesis of graphene with properties fitting for the specific application, what's more, this circumstance is liable to proceed for the next decade or if nothing else until each of graphene’s many potential applications meets its own particular requirements. Currently there are most likely a dozen of techniques being used and developed to synthesis graphene of different dimensions, quality and shapes. \(^{83,84}\)

**My thesis organization:**

In the next chapter of my thesis, one can find the exfoliation of graphene in the liquid phase exfoliation using the shear mixing method. During my stay in the Uppsala University Sweden, I was involved in the experiments with the liquid phase exfoliation method of graphene and modelling the production mechanism of graphene. In this chapter I have presented the detail of the protocols involved in the synthesis of graphene and the modelling of the surface energies of Ethanol, Cyclohexanone, NMP w.r.t to graphene and the graphical representation of reduction of the graphene flake thickness with some shear mixing parameters.

In the third chapter, I have explained the exfoliation of graphite by using the sound waves in the liquid solution and finally the advantages and disadvantages of both the exfoliation methods. And I have calculated the time for exfoliation of single layer. Finally, the conclusion is summarized for both methods and some future outlook is presented.
Chapter # 2

Shear exfoliation of Graphene

Introduction of the process
Shear mixing is a process of exfoliation of the graphite in the liquid phase by using the shear force mechanism. In this process, a machine (Silverson model L5M mixer) is used to generate high shear force. The Silverson model consists of manual control system, rotor and stator part (see figure 1) and the purpose of this machine is to mix the solution of solvent and graphite and shear the graphite. In shear mixing process, the graphite is mixed with the organic solvent like ethanol, Cyclohexanone and NMP.

![Figure 1](image.png)

Figure 1: Shear mixing machine. a, Image of shear mixing operator. b, Rotor. c, clear view of functioning part. d, different shape of stator. e, combination of Rotor and stator. f, exfoliated samples

Here, we can say that high-shear mixing is a scalable alternative to the sonication process for the peeling of layered crystal of graphite. Shear mixing is already generally used to disperse nanoparticles in solvents. It includes separating of microparticle agglomerates that are weakly attached compare with the intersheet binding strength in graphite. The exfoliation of graphite or layered material that incorporates shear mixing as a part of the procedure is reported in different articles. In shear mixing, the layered material is initially swelled by intercalation, significantly reducing the interlayer binding strength. The shear mixing exfoliated the crystal material graphite to give dispersed nanosheets. However, shear mixing method just limiting the rate step (Time) for intercalation and exfoliation, increases the potential for scale-up. The shear mixing process has much more ability to exfoliate the untreated graphite crystal material into liquid solution. In addition, Shear mixing process utilizes less power densities as compared to Ultra-sonication method.
Mechanism of the process

The shear mixing exfoliation method works for the exfoliation of graphene in liquid phase. To understand the mechanism of exfoliation in liquid we have to first understand some term like cohesive force, surface energy and viscosity. The cohesive force is defined as the attraction of one molecule toward other molecule which held together the molecules of the atom in the bulk material in the layers. Surface energy is defined as the imbalance energies at the top surfaces of the materials such as liquid or solid. In the bulk material,

![Figure 2: Attractions in the Layers of graphene](image)

the energies in centre remain same so every molecule get force exerted equally from surrounded molecules. The molecules present in the top layer of material have different energies because top layer remain in the contact of the atmosphere and experience the imbalance energies in the surface. In term of graphite, when solid graphite mixed with the solvents, they attach into the layers of graphite to reduce the Vander Waal force in between layers (see figure 2). Actually, the total energy ($E_T$) required to exfoliate the graphite in the liquid is the combination of the Vander Waal forces ($E_{vwf}$) and the change of the surface energies ($E_s$).

$$E_T = E_{vwf} + \Delta E$$

$$E_T = E_{vwf} + [E_g - E_s]$$

Where,

$E_T$ is the total energy requires for exfoliation,

$E_{vwf}$ is the Vander Waal force between the layers of graphite,

$E$ is the changes in surface energies,

$E_s$ is the surface energy for the mixing organic solvent
The exfoliation of graphite requires to overcoming these energies. Generally, the graphene layers are attached with each other by weak Vander Waal attraction and that attractions are strong enough to exfoliate the graphene single layer from the graphite.

**Experimental procedure**

We use the shear mixing process to exfoliate the graphite for production of graphene. For this we mix the graphite powder and organic solvent in the beaker with a specified weight ratio. We also add some polymer stabilizer along with them, in order to keep the exfoliated graphene flakes stable inside the dispersion. The beaker is placed at the bottom stage of the shear mixer. By controlling the setup, the rotor (outside diameter 32 mm) is inserted into the beaker. The speed of the rotor can be varied using the setup monitor. The maximum rotor speed that can be obtained with full load is 8000 rpm. In order to see the changes of thickness and the lateral diameters of the exfoliated graphene flakes on the types of solvents generally used, a wide range of solvents with different surface energies are used in our study. The speed of the rotor is varied from 1000 rpm to 6000 rpm. The process was performed for a fixed duration of 20 min. After each shear mixing completion, the supernatant obtained from the top part of the dispersion is spin coated on Si/SiO$_2$ substrates and the morphology of the films are characterized through atomic force microscopy technique using non-contact mode. The thickness and the lateral diameters of the flakes are evaluated through this process.

**Experimental results and discussions**

The shear mixing is first performed in ethanol based exfoliation. Initially the thickness of graphite flakes was 1μm. When the shear speed is increases from 0 to 1000 rpm; the thickness and the diameter of graphene flakes get affected and the graphene flake thickness is reduced from 1000 nm to 740 nm. When the shear speed varies from 1000 to 5000 rpm, the thickness is reduced sharply with the increasing speed and reduced down to ~100 nm. The diameter is also reduced from 20,000 nm to 2900 nm. After that the shear speed doesn’t affect the exfoliation process and the thickness as well as the diameters remain constant (see figure 4).

In Cyclohexanone based exfoliation, when the shear speed is increase from 0 to 1000 rpm, the thickness and the diameter are reduced. The thickness is reduced from 1000 nm to 500 nm. When the shear speed is increased from 1000 to 5000 rpm, the thickness is sharply reduced down to 70 nm. The diameter is also reduced from 20,000 nm to 250 nm. After that the shear rate don’t not affect the thickness and diameter (see figure 5).

Similarly, when the shear mixing process is used with the NMP, the shear speed affects the thickness and the diameter. When shear speed increases from 0 to 1000 rpm, the thickness is reduced from 1000 nm to 400 nm. When the shear speed is increased gradually from the 1000 to 5000 rpm, the thickness and diameter are sharply reduced down. The thickness is reduced down and the minimum reduced thickness obtained is 10 nm for 5000 rpm speed. On the other hand the diameter is also reduced from 20,000 to 250 nm. After that the shear speed doesn’t affect the exfoliation process and the thickness as well as the diameter remains constant. The NMP is greatly affecting the shear mixing process, and the thickness and diameter reduce more as compared to the ethanol and cyclohexanone (see figure 6).
When the shear rate is increased gradually, the thicknesses as well as the diameters of the graphene flakes are reduced for all the above mentioned organic solvents. There is a clear trend of sharp reduction of the thickness and the diameters after 1000 rpm and we found a critical speed of 5000 rpm above which there is no further exfoliation. If we compare three organic solvents, we can see through graph that the ethanol shows the less exfoliation (see Figure 4). The cyclohexanone shows the moderate exfoliation as compared to ethanol and NMP (see figure 5). NMP based exfoliation shows better exfoliation rate as compared to the ethanol and cyclohexanone (see Figure 6).

![Graph 1](image1)

**Figure: 4** Variation of exfoliated graphene flake thickness and lateral diameters with increasing shear mixing speeds. The variation is for ethanol based exfoliation.

![Graph 2](image2)

**Figure: 5** Variation of exfoliated graphene flake thickness and lateral diameters with increasing shear mixing speeds. The variation is for cyclohexanone based exfoliation.
Theoretical modelling of the experimental results

The shear mixing mechanism works on the force of friction and applied force. When we use the shear mixing process, rotor rotates and applies force into the solution. Initially, the static friction occurs when the applied force through the rotor exerted into liquid solution (solid graphite and organic solvent), the friction produced into the solution. With the increase of the shear mixing speeds, the applied rotational force faced by the flakes increases as well, this allows the sliding of the graphene layers between themselves. As a results, the friction between the two adjacent graphene layers increases linearly as shown in Figure 3.1, which is termed as the static friction. Due to increase of the friction with the applied force, it is hard to separate the individual layers form each other and almost no exfoliation occurs in this region (from F0 to F1 as shown in Figure 3.2). In our practical experiments, we did not see any exfoliation when the shear mixing speeds are increased slowly from 0 to 1000 rpm. We suppose the frictional force is so huge in this region, therefore basically it is impossible to separate the layers of graphene. As a result, there is no reduction of either thickness or size of the flakes as shown in figure 3.3.

When further increase of the applied force, the frictional force starts to reduce and therefore the exfoliate occurs. We can see than exponential decay of the frictional force with the applied force in the region between F1 and F2 (Figure 3.1). In this period the graphene layers start to slide between each other and with the increase of the applied force they separate from each other. We can say that the exfoliation starts from this region and from our practical measurements, it occurs after 1000 rpm. As a result, both the thickness and the size of the flakes reduce exponentially as we have shown in Figure 4, 5 and 6.

With further increase of the applied force, the frictional force becomes constant, which means easy exfoliation of the layers, however, there is a limit of the exfoliation of the layers which depends on the surface energies of the solvents used, we can see a stable thickness and the size of the flakes after a certain speed of 5000 rpm (corresponds to F2 in the Figure 3.2).
Figure 3.1: Graph of force of friction and applied force

http://www.sciencehq.com/physics/frictional-force.html

Figure 3.2: Graph of Exfoliation and applied force

Exfoliation

Thickness
Figure 3.3: Graph of force of friction and applied force

The surface energies are calculated through the following calculation,

\[
\dot{\text{r}}_{\text{min}} = \left[ \frac{\sqrt{E_{\text{graphene}}} - \sqrt{E_{\text{solvent}}}}{\eta \cdot l} \right]^2
\]

\[
\dot{\text{r}}_{\text{min}} = \left[ \frac{\sqrt{E_{\text{graphene}}} - \sqrt{E_{\text{solvent}}}}{\eta} \right]^2 \cdot \frac{1}{l^2}
\]

\[
l = \left[ \frac{\sqrt{E_{\text{graphene}}} - \sqrt{E_{\text{solvent}}}}{\eta \cdot l} \right]^2 \cdot \frac{1}{\dot{\text{r}}_{\text{min}}}
\]

\[
l = \frac{\sqrt{E_{\text{graphene}}} - \sqrt{E_{\text{solvent}}}}{\eta} \cdot \frac{1}{\sqrt{\dot{\text{r}}_{\text{min}}}}
\]

\[
l = \frac{\sqrt{E_{\text{graphene}}} - \sqrt{E_{\text{solvent}}}}{\eta \cdot \sqrt{\dot{\text{r}}_{\text{min}}}} \quad \text{----------------(1)}
\]

Where,

\( \dot{\text{r}}_{\text{min}} \) = Shear rate (s\(^{-1}\))

\( E_g \) = Surface energy of graphene, (N/m)

\( E_s \) = Surface energy of solvent, (N/m)

\( \eta \) = Solvent viscosity, (Pa.s)

\( l \) = Flake length, (m)
**Viscosity of Solvents**

The viscosity of solvent is defined as the thickness of the solvents which resist to flow. It is also an important term for the exfoliation of graphite in the liquid. The viscosity of the liquids which we are using in our experiments is given below.

<table>
<thead>
<tr>
<th>Viscosity of solvents (Pa.S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethanol</td>
</tr>
<tr>
<td>Cyclohexanone</td>
</tr>
<tr>
<td>NMP</td>
</tr>
</tbody>
</table>

The surface energies of the three solvents e.g. Ethanol, Cyclohexanone and NMP are very important when we talk about the exfoliation of graphite. We have taken the model reference from the literature 85 (Scalable production of large quantities of defect-free few-layers graphene by shear exfoliation in liquids) and calculated the surface energies of the solvents.

From equation (1), the shear rate is the mixing rate of the solution and it is given as,

\[
\dot{\gamma}_{\text{min}} = \frac{2 \pi N D}{\Delta R}
\]

where,

\( N \) = number of revolution per min,
\( D = 0.0320 \text{ m} \),
\( \Delta R \) = gap of rotor-stator,

So,

\[
\dot{\gamma}_{\text{min}} = \frac{2 \times 3.14 \times 83.3334 \times 0.0320}{0.0001}
\]

\[
\dot{\gamma}_{\text{min}} = 167467 \text{ s}^{-1}
\]
this is the value of the shear rate of all solvents for 5000 rpm. Now for the calculation of surface energy of Ethanol $\sqrt{E_{\text{Ethanol}}}$, by rearranging the equation (1), we get

$$\sqrt{E_{\text{Ethanol}}} = \sqrt{E_{\text{graphene}} - \sqrt{r_{\text{min}}} \cdot \eta \cdot l}$$

$$= \sqrt{0.0763} - \sqrt{167467} \cdot 0.00107 \cdot 0.000007$$

$$= 0.2645 - \sqrt{0.001254}$$

$$= 0.2645 - 0.03541$$

$$\sqrt{E_{\text{Ethanol}}} = 0.22909$$

Take the squaring on both sides,

$$(\sqrt{E_{\text{Ethanol}}}^2) = (0.22909)^2$$

$$E_{\text{Ethanol}} = 0.0524 \text{ N/m}$$

$$E_{\text{Ethanol}} = 52 \text{ mJ/m}^2$$

By using the similar calculation and procedure, the surface energies of the cyclohexanone is calculated as 62 mJ/m$^2$ and for the NMP is 69 mJ/m$^2$.

**Conclusion of chapter 2**

1. We have exfoliated graphene flakes out of graphite from a novel method which is shear exfoliation technique. In this process, the applied shear force helps to separate the graphene layers by overcoming the vander Waal’s force of attraction.

2. We have shown the variation of the thickness and the lateral diameters of the flakes with shear mixing speeds.

3. We have defined a critical shear mixing speed beyond which there is no more exfoliation.

4. Using an available shear mixing mechanism, we have extracted the surface energy values of some well known solvents usually used for exfoliation of graphene.

5. We have shown a correlation between frictional force and the reduction of thickness.


Chapter # 3

**Sonication of graphite**

**Introduction of the process**

Sonication is another method for exfoliation of graphite layers into the solution. It is based on the sound waves in which the solution is placed in the ultra-sonication bath. The solution kept in the beaker, and placed in the sonication bath. The sonication bath exerted the pressure in the beaker solution and then the solution in which the organic solvent and the graphite are present experiences the force from the sonication bath which causes reduction of the flake thickness. It is slow process for the exfoliation. The result from the sonication process for three organic solvents ethanol, cyclohexanone and NMP are given below.

**Experimental procedure**

We use the sonication mechanism in the liquid phase to exfoliate the graphite into the solution for production of graphene. For this process, we mix the graphite powder, organic solvent and polymer stabilizer with specific quantity into the beaker and keep the beaker into the sonication bath. We add the polymer stabilizer into solution because to keep the graphene flakes stable into the solution. The sonication bath works on different frequencies. We used 20 KHz frequency to disperse and exfoliation of the solution. The sonication bath transfers the energy into the water present into the bath then the water exerted the pressure to the breaker. The pressure then transmits in to the solution, disperse and exfoliate the graphite into the solution. This process is time consuming and produces the graphene into the liquid. The process was performed at different times. After the completion of ultra-sonication, we take the small amount of supernatant from the top part of the solution to spin coat it on the substrate of Si/ SiO₂. Then we characterize the sample through the atomic force microscopy technique.

**Experimental results and discussions**

The ultra-sonication technique in the liquid phase exfoliation is first accomplished in ethanol based exfoliation. In this process, initial thickness of flakes of graphite was 1μm (1000 nm). In order to increase the ultra-sonication time (hour), the thickness of graphite flakes is decrease. Briefly, when the ultra-sonication time is increased from 0 to 300 hour, the thickness of the graphite flakes is reduced down from 1000 nm to 80 nm for ethanol. After that the ultra-sonication time doesn’t affect the exfoliation process and the thickness remains constant (see Figure 1).

For the cyclohexanone, when the ultra-sonication time increases from 0 to 300 hour, the thickness of graphite flakes is get affected through the sonication time. The thickness is reduced down from 1000 nm to 40 nm. After this thickness, there is no further reduction of the thickness (see figure 2).
In NMP based exfoliation, the affect is much severe. When ultra-sonication time increases from 0 to 300 hour, the thickness is reduced down from 1000 nm to 10 nm. After this point, it doesn’t affect the exfoliation process and the thickness remains constant. (see figure 3).

Figure 1: Ultra-sonication data for Ethanol solvent
Figure 2: Ultra-sonication data for Cyclohexanone solvent

Figure 3: Ultra-sonication data for NMP solvent
Comparison of the both methods

We have used to different methods in liquid phase exfoliation for production of graphene. But methods have some advantages and disadvantages. If we compare both methods, according to some parameters, we have some conclusion given below.

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Shear Mixing Exfoliation</th>
<th>Ultra-sonication Exfoliation</th>
</tr>
</thead>
<tbody>
<tr>
<td>Time</td>
<td>Less time</td>
<td>Longer time</td>
</tr>
<tr>
<td>Thickness of final product</td>
<td>same</td>
<td>same</td>
</tr>
<tr>
<td>Scalability</td>
<td>Yes</td>
<td>No</td>
</tr>
<tr>
<td>Concentration of final product</td>
<td>same</td>
<td>same</td>
</tr>
</tbody>
</table>
Theoretical modelling of the experimental results

Here is the calculation of one layer exfoliation. The distance between the graphite layers is 0.34 nm and initially the thickness of graphite is 1000 nm and we notice that the linear exfoliation happens up to 300 hours and the thickness reduces at 80 nm for ethanol.

The exfoliated thickness at 300 hour is = 1000 - 80

= 920 nm

We know that the distance between the layers is 0.34 nm.

The number of layers exfoliated at 300 hour is given as

Number of layers exfoliated = \(\frac{920}{0.34}\)

Number of layers exfoliated of ethanol = 2705

So,

One layers exfoliation time (min) is = \(\frac{300 \times 60}{2705}\)

One layers exfoliation time is = 6.65 min for ethanol

Now the remaining layers at 80 nm = \(\frac{80}{0.34}\)

Remaining layers = 235

So now we can know that the total number of layers \(L_T\) at initial 1000 nm thickness is

\[ L_T = 2705 + 235 \]

\[ L_T = 2940 \]

On the other hand, if we calculate the exfoliation of single layer time with same method for Cyclohexanone and NMP, it is given as,

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Time(min)</th>
<th>Reduced thickness(nm)</th>
<th># of layers exfoliated</th>
<th>1 layer exfoliated time</th>
<th>Remaining layers</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cyclohexanone</td>
<td>300</td>
<td>960</td>
<td>2823</td>
<td>6.37</td>
<td>117</td>
</tr>
<tr>
<td>NMP</td>
<td>300</td>
<td>990</td>
<td>2911</td>
<td>6.1</td>
<td>29</td>
</tr>
</tbody>
</table>
We can see the exfoliation time for the one layer from the graphite flakes is reduces when the surface energy value of the corresponding solvent is close to that of the graphene. Since, from our previous chapter, we concluded that the surface energy of NMP is much close to graphene and from this chapter we concluded that the time required for one layer exfoliation is minimum for NMP, we can correlate both conclusions.

**Conclusion of chapter 3:**

We can see the exfoliation time for the one layer from the graphite flakes is reduces when the surface energy value of the corresponding solvent is close to that of the graphene. Since, from our previous chapter, we concluded that the surface energy of NMP is much close to graphene and from this chapter we concluded that the time required for one layer exfoliation is minimum for NMP, we can correlate both conclusions.

1. We have exfoliated graphene flakes out of graphite through the ultra-sonication technique. In this process, the applied sound energy helps to separate the graphene layers by overcoming the vander Waal’s force of attraction.

2. We have shown the variation of the thickness with ultrasonication time

3. We have defined a critical ultrasonication time, above which there is no more exfoliation.

4. We have calculated the single layer exfoliation time using the data obtained from the measurements.
Conclusion

In this project, we have used to different methods for the production of graphene from graphite. The methods are based on the liquid phase exfoliation. Through these two methods we have come to know that the surface energy is one of the main parameters for the exfoliation. We used three different organic solvents for the exfoliation. These were Ethanol, Cyclohexanone and NMP. The liquid which has surface energy close to the graphene is better for the exfoliation. These two methods produced graphene in which the shear mixing exfoliation takes less times for the production of graphene on the other hand, the ultra-sonication consumes more time.

If we compare both methods, the shear mixing exfoliation is more scalable method because it can produce large quantity of flakes compared to the ultra-sonication based exfoliation.

Future work

Our work gave a solid indication of the choice of solvent requires for the efficient exfoliation. In future, efforts should be devoted to use the track presented here to exfoliate the graphene flakes efficiently with further optimization of the methods.

Finally a way should found to produce large amount of high quality graphene through both methods in the liquid phase exfoliation so that we can use it in our daily life application.
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