<u>Novel, Scalable, Sustainable Graphene Synthesis:</u> <u>Electrolytic Exfoliation</u>

(Finding the Optimum Range of Electrical Current)

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Abstract:

Graphene is a novel nanomaterial, only recently discovered in 2004. It has prompted multiple scientific breakthroughs in a variety of fields, proving transform industries at a large scale, such as electric vehicles, batteries, solar panels, protective coatings, etc. Historical methods of graphene synthesis, including mechanical and chemical exfoliation and chemical vapor deposition (CVD), present challenges such as high costs and are also environmentally unfriendly, posing sustainability concerns.

Understanding graphene manufacture through a sustainable lens is extremely important for graphene's longevity. This study aims to explore the optimal conditions for electrolytic exfoliation, a sustainable, scalable, and simple method for graphene production, by determining the optimum electrical current to maximize both quantity and quality of graphene yield, verified through qualitative observations and subsequent analysis using Raman Spectroscopy and SEM/EDX. Results indicated that an electrical current of 0.2–0.3A yielded the most substantial and high-quality graphene. This research highlights the potential for optimizing the electrolytic exfoliation process to produce graphene sustainably and efficiently, showing promise for widespread industrial application and further research into refining these methods for cleaner, sustainable and more effective graphene production.

Aim:

The aim of this study is to determine the optimum level of electrical current required to perform electrolytic exfoliation at, as a sustainable method for graphene manufacture.

A. Introduction:

Graphene is a relatively new 2-dimnesional allotrope of carbon, discovered only in 2004 (20 years ago) by scientists at the University of Manchester (*Graphene: The Wonder Material of the 21st Century* | *Topics* | *European Parliament, 2015*). It is obtained from its parent allotrope, graphite. Graphite is a 3-dimensional entity, composed of multiple layers of graphene, held together by strong Van der Waal intermolecular forces. When graphene is produced by extraction from graphite, it exists as a one-atom-thick planar sheet of sp² carbon atoms arranged in a hexagonal lattice.

The model of graphite and graphene can be better understood using an analogy of a stack of papers. Each singular sheet of paper represents a sheet of graphene, whereas the stack of sheets packed close together represents graphite. The chemical structures of graphite and graphene are shown in the labelled figure (Fig. 1) below.



Fig. 1: Graphite and Graphene

Graphene, the transparent 2D nanostructure, is classified as a 'wonder material' due to its amazing physical properties, including high strength, thermal (3,000 – 5,000 W/mK) and electrical (10 – 1,000 s/cm) conductivity, elasticity and mechanical flexibility (*Graphene Thermal Conductivity* - *Introduction and Latest News* | *Graphene-Info, n.d.; O'Neill et al., 2021*). It has a high Young's Modulus of around 1,100 GPa and high fracture strength of 125 GPa (*Fig. 3 Chart of Young's Modulus as a Function of Density Comparing.,n.d.*). Young's Modulus establishes the relationship between stress acting on a substance and the strain it produces, while fracture strength indicates the maximum weight, a material can withstands before it cracks. Further, it is water impermeable and extremely light; one square meter of graphene weighs only 0.77mg (*Admin_Fourmizz, 2023*). Conversely, graphite has considerably lower fracture strength of only 88GPa (*Yi et al., 2021*) and a maximum thermal conductivity of 2000 W/mK (*Carbon, 2024*). It is important to note that graphene also has a higher electrical conductivity due to higher electron mobility, being a 2d substance. Hence, graphene enhances graphite's physical properties, making it extremely unique and useful.

B. Practical Applications:

Graphene has widespread applications that cover all gametes of life, especially because it is a single substance that possesses all the properties described above. Some applications include its use in biosensors, batteries, protective coatings, water filtration, and solar panels, among others. Below are a few examples of how graphene succeeds in some of these fields.

B.1 Biosensors

To begin with, graphene is highly suitable for biosensors due its high sensitivity, which helps detect diseases, pathogens, or biomolecules much faster – depending on their specific use and context. Graphene, being a 2D material, has an enormous surface area, which provides a high density of binding sites for biomolecules, enhancing the sensitivity of the biosensor. Furthermore, high electronic mobility in graphene allows graphene biosensors to detect very low concentrations of analytes, enabling the detection of biomolecules at trace levels. Research by Prof. Jinglei Ping and A.T. Charlie Johnson shows how Graphene Field Effect Transistors (GFETs) are especially useful in the development of scalable biosensors that help detect changes in the human body with DNA, or even to detect serious diseases such as HIV (*Ping et al., 2016*). The biosensors are functionalized with single-stranded probe DNA and can detect DNA hybridization with high sensitivity and selectivity, making biosensors a promising technology for rapid and accurate DNA detection, among its other uses within biotechnology and biosensors.

B.2 Energy

With respect to Lithium-ion batteries (LIBs), graphene increases their reversible capacity, which is larger than that of the commercial anode material (graphite) due to its high surface area, electrical conductivity, and chemical stability. The graphene layer acts as a protective barrier that prevents the dissolution of the cathode material into the electrolyte, while its high thermal conductivity helps dissipate heat more effectively, thus extending the life of the battery. As per Newark Electronics, the battery life of a typical LIB is about 300 to 500 charge cycles (two to three years) (*Tektronix, n.d.*). Conversely, the typical lifespan of a graphene enhanced LIB is often far longer, around 1,000 to 2,000 charge cycles (five to seven years) (*Ali et al., 2022; Lavagna et al., 2020*). Graphene-enhanced LIBs also potentially reduce the reliance on toxic materials and rare metals used in traditional batteries. This makes them more environmentally friendly and sustainable in the long term.

Another similar application of graphene is in solar panels. Graphene's high electrical conductivity, coupled with its lightweight nature make it a lucrative option to enhance the performance of photovoltaic cells. It is used as a transparent electrode to better facilitate electron transport, leading to higher power conversion efficiencies and longevity (*Mahmoudi et al., 2018*). Thus, the use of graphene is solar panels could contribute to a cleaner environment and more efficient, sustainable energy options.

B.3 Coatings

Lastly, Graphene has been found very useful for improving the properties of protective coatings. Graphene creates pathways that are very tortuous, preventing water and oxygen molecules and/or chemical agents from diffusing to the surface of metal-based materials, resulting in metal protection against oxidation and corrosion (*Graphenemex, 2023*). Thus, graphene has a positive role in enhancing paint properties such as corrosion protection, strength, reduced permeability and antistatic properties. Very small amounts of graphene (0.5-1%) are enough to foster a significant positive effect in the paint system. (*Aneja et al., 2015*).

C. Methods of Manufacture:

There are many possible methods to manufacture graphene, and they fall into two categories the 'top down' and bottom up approach.

The top down approach involves synthesizing graphene from its parent allotrope, graphite. To reiterate, graphite is a highly layered material, where each graphene layer is held by strong Van der Waals forces. Manufacturing graphene via the top down approach involves separating graphene layers from this layered material. Methods to do this include Mechanical Exfoliation, Pressure Exfoliation, Chemical Exfoliation, and Electrolytic Exfoliation. Conversely, the bottom up approach involves using chemicals such as methane and hydrogen to produce graphene in its pure form, or as a compound. An example of this is Chemical Vapor Deposition (CVD), which is the most popular method to produce graphene today.

C.1 Mechanical Exfoliation

Mechanical Exfoliation, also called the Adhesive-Tape method, involves repeatedly peeling off highly oriented pyrolytic graphite (HOPG) from a substrate, usually a sponge, using scotch tape (*Reeves et al., 2010*). This results in a single sheet of graphite getting stuck to the scotch tape, and is separated from the graphite, thus classifying it as top down. The mechanical forces applied when pulling the tape apply stress, thus breaking the strong Van der Waal's forces that hold the graphene sheets together. While this cost effective method helps produce high quality graphene, it is sometimes inconsistent and has low yield, which hampers scalability and widespread industrial use.

C.2 Pressure Exfoliation

Pressure Exfoliation can be explained using the analogy earlier introduced in this study, of a stack of papers. By blowing on this stack of papers, the sheets slide over each other, and separate from the stack. Similarly, by applying high pressure to graphite, the sheets of graphene slide over one another and separate into monolayer nanostructures of graphene. Thus, this is also a top down approach. Unlike Mechanical Exfoliation, this method often produces high quantities of graphene (high yield), achieving scalability. Unfortunately, it requires large amounts of energy and may produce inconsistent layers of graphene, which may negatively affect the quality of graphene produced.

C.3 Chemical Exfoliation

Chemical Exfoliation, by Hummer's Method, involves oxidation of graphite to produce graphene, and is a third example of a top down approach. It entails reacting graphite with concentrated Sulfuric Acid (H_2SO_4) in the presence of Sodium Nitrate ($NaNO_3$) and Potassium Permanganate ($KMnO_4$), which act as catalysts, to obtain Graphite Oxide ($Yu \ et \ al., 2016$). H_2SO_4 intercalates between the layers, thus separating them. The Graphite Oxide then goes through sonication to produce Graphene Oxide. Sonication is the process of using ultrasound to separate materials into fine nanoparticles, which is usually difficult using common stirring methods. Lastly, the graphene oxide undergoes chemical or thermal reduction to produce monolayer graphene. Like Pressure Exfoliation, this method is scalable, as the reaction can be performed using large quantities of reactants. However, due to its chemical nature, the product is subject to chemical residue. To eliminate this, intensive purification may be required, which is often expensive.

C.4 Chemical Vapor Deposition (CVD)

The most common method, CVD, involves the decomposition of a hydrocarbon gas, typically methane (CH_4) into carbon atoms, while hydrogen is released as a by-product. It occurs at very high temperatures, ranging from 800°C to 1,000°C (*Jang et al., 2015*). The carbon atoms then arrange themselves into a graphene layer on a substrate, which is often copper. The reaction is:

$$CH_{4(g)} \rightarrow C_{(s)} + 2H_{2(g)}$$

Thus, the graphene is built up using raw materials, classifying it as a bottom up method. It is the most widely used due to its ability to produce high-quality, uniform graphene sheets in a more controlled manner. However, it is a complex process requiring costly equipment, and may thus be

unfeasible in rural or developing areas. The use of chemicals may also contribute to it being an unsustainable and environmentally unfriendly production method.

C.5 Electrolytic Exfoliation

Lastly, Electrolytic Exfoliation involves the separation of graphene sheets from graphite using electrochemical principles. The method is described in detail in the following section. It is a simple, top down, scalable method that produces high quantities of graphene apt for industrial use. It is also less environmentally harmful as it does not release nor involve the use of any harmful chemicals, unlike the two chemical methods described above. Furthermore, it especially offers a sustainable method for graphene production if the electrolytic cell is powered by a clean energy source. However, it may sometimes produce inconsistent sheets of graphene. This relatively new method of production has not been studied enough yet. Its inconsistency drawbacks can be rectified by choosing the correct electrical current for the power supply in the electrolytic cell. Thus, this study will investigate Electrolytic Exfoliation, aiming to identify how to maximize the amount and quality of graphene produced by varying electrical current.

D. Electrolytic Exfoliation:

Electrolytic Exfoliation, as mentioned in the previous section, is an electrochemical process in which monolayer graphene sheets are extracted from a block of graphite. It makes use of an electrolytic cell where the electrolyte is aqueous, organic or an ionic liquid. Fig. 2 shows a typical setup.



Fig. 2: Typical Setup

In this study, an AR Grade of Ammonium Sulfate $((NH_4)_2SO_4)$ combined with 2,2,6,6tetramethylpiperidine-1-oxyl (TEMPO) is used as an aqueous electrolyte. It is chosen as an alternative to harsh acidic electrolytes such as sulfuric acid (H_2SO_4) , making the process safer. TEMPO is an oxidizing agent, used to prevent the graphene formed from oxidizing to form graphene oxide. As a free stable radical, it helps stabilize the radical species generated during the exfoliation process. It does this by creating a layer on the graphene to preserve it in its pure carbon form.

Graphite is made the anode (positive electrode) and platinized platinum is made the cathode (negative electrode), where both electrodes are inert. The electrodes are connected to a basic electrochemical cell, which acts as the DC power supply for the experiment.

At the anode, oxidation occurs, which is the loss of electrons. The general equation for this reaction, assuming M is the anodic species, is: $M_{(s)} \rightarrow M^+_{(aq)} + e^-_{(aq)}$. Presumably, this would mean the carbon atoms in graphite are oxidized to produce carbon ions and electrons. However, graphite is inert and does not take part in the reaction. In that case, oxygen is produced instead:

$$2H_2O_{(l)} \rightarrow O_{2(g)} + 4H^+_{(aq)} + 4e^-$$

At the cathode, reduction occurs, which is the gain of electrons. A platinized platinum electrode is used because platinum is inert, i.e. does not take part in the reaction itself. It is platinized (coated with platinum back) to increase its surface area, as the coating results in a mildly rough surface. This increases the efficiency and rate of the reaction, as the reaction site is greater. As platinum is inert, the H^+ ions in the electrolyte are reduced at the cathode to produce hydrogen gas. This is the Hydrogen Evolution Reaction (HER), the chemical equation being:

$$2H^+_{(aq)} + 2e^- \to H_{2(g)}$$

The production of hydrogen gas results in effervescence. These bubbles not only regulate electron flow in the cell, but their movement in the electrolyte ensures its consistency.

At the anode, produced oxygen combines with carbon atoms in the graphite to form various oxygencontaining functional groups including carbonyl, carboxyl, etc. This disrupts the typical structure of graphite layers, as delocalized electrons are used to form these chemical bonds. This results in the typical sp^2 hybridization being lost, and instead there exists sp^3 hybridization between carbon atoms. This disruption in structure results in greater spacing between the graphite layers, and is the first step towards breaking the strong Van der Waals forces that holds the layers together. Next, anions (negative ions) present in the electrolyte, in this case sulfate ions (SO_4^{2-}) , move towards the anode (positive electrode) due to electrostatic forces of attraction between opposite charges. These ions intercalate in the graphite, by moving themselves between the layers that make up the graphite. This process weakens the Van der Waals forces even further, eventually resulting in exfoliation (separation) of monolayer or few-layer graphene. Intercalation occurs in stages, where initial stages result in few-layer graphene, whereas final stages produce monolayer graphene. This is diagrammatically represented in Fig. 3, where the n^{th} stage represents the number of layers in each layer of graphene.



Fig. 3: Intercalation in Stages (Inaba, 2009)

The produced graphene falls to the bottom of the electrolytic cell. It must then be collected, dried, and tested before it is ready for industrial use.

E. Experimental Process:

E.1 Apparatus

A DC Power Supply (battery cell), glass beaker, acrylic lid, stirrer and insulated wires were used. No special equipment was required, stressing the simplicity of this process.

E.2 Materials and Chemicals

An AR grade of Ammonium Sulfate ($(NH_4)_2SO_4$), 2,2,6,6-tetramethylpiperidine-1-oxyl (TEMPO), graphite rod, and platinized platinum rod, and PTFE membrane filter were used. These were available at the laboratory where the experiment was conducted (see acknowledgements).

E.3 Variables

The independent variable was the Electrical Current of the battery cell (<0.1A, 0.1-0.2A, 0.2-0.3A, 0.3-0.4A, >0.4A). This was varied using settings on the battery cell. Corresponding automatic voltages were accepted.

The dependent variable was the amount and quality of graphene produced.

Variables that were kept constant include:

- Size of Beaker (750ml)
- Composition of Electrolyte:
 - i. Amount of Tempo Added (50mg)
 - ii. Conc. of Ammonium Sulfate (0.05M)
- Mass of Electrodes (20g Graphite, 5g Platinum)
- Distance between Electrodes (2cm)
- Volume of Electrolyte (500ml)
- Time period (1 week)

By keeping these variables constant, the experiment ensures that any changes in the exfoliation process can be attributed to electrical current (and respective automatic voltages), to ensure valid and reliable results. Details are outlined in the next section (E.4).

E.4 Method

The electrolytic exfoliation was performed in a two electrode system, where a graphite rod was using as the anode and platinized platinum was used as the counter electrode (cathode). Both electrodes were placed parallel to one another at a fixed distance of 2cm. The electrolyte for the graphite exfoliation was prepared by dispersing ammonium sulfate salt (0.05M, 0.660 g) and TEMPO (50 mg) in 50 mL of DI water in a beaker.

A 750mL beaker was used. For the process to succeed, the water level had to be high enough for a significant portion of the electrodes to be immersed in it. Thus, maintaining the concentration of 0.05M, 6.60g of ammonium sulfate salt and 0.50g of TEMPO were used in 500mL of distilled water.

In order to make the preparation of the electrolyte more efficient, the TEMPO was first ground into a fine powder using a mortar and pestle, then weighed, and then put into the beaker. The contents of the electrolyte were then stirred using a glass rod until the electrolyte was homogenous and its contents dissolved. The electrolytic cell was then set up.

The desired current was then set on the battery cell. The corresponding applied voltage was automatically determined by the battery cell, and accepted. Fig. 4 below shows the electrolytic setup for experimental group 0.2-0.3A.



Fig. 4: Experimental Setup

This setup was left for one week, and qualitative observations recorded on Day 1, 3, 5, and 7 (results in section F). This process was repeated for each of the other current levels (<0.1A, 0.1 0 - 0.2A, 0.3 – 0.4A, >0.4A)

If applicable, once the exfoliation was complete, a part of the graphene-containing solution was poured into a watchglass. It was placed into an oven at 50°C overnight to evaporate the electrolyte. Once done, the collected graphene was washed with distilled water to remove any chemical residues from the electrolyte. It was then placed back into the oven in the same conditions. Once only a dark gray powder remained, it was collected and sent for testing. A $0.2 \mu m$ PTFE membrane filter was used through this process to remove impurities.

F. Raw Data:

Day:	Observations				
	<0.1A	0.1 – 0.2A	0.2 – 0.3A	0.3 – 0.4A	>0.4A
1	No Change	No Change	No Change	Vigorous	Vigorous
				Effervescence,	Effervescence,
				Solution Black	Overspilling,
					Solution Black
3	No Change	No Change	Small Grey	Overspilling	N/A
			Chunks		
			Suspended		
5	No Change	No Change	Small Graphene	N/A	N/A
			Chunks Settled		
7	No Change	Small Graphene	Solution Black	N/A	N/A
		Chunks Settled			

Table 1: Instant Observations on the effect of Varying Electrical Current

G. Data Analysis

An electrical current <0.1A did not yield any graphene, and the experiment was unsuccessful. This suggests that the current was too low to prompt the electrolytic exfoliation process to begin. Fig. 5 shows the setup on day 7.

Further, while an electrical current of 0.1 - 0.2A did yield graphene, the amount synthesized was almost insignificant. Regardless, the drying process was executed with this graphene sample. However, the amount was too less, and thus ineligible for testing. This highlights the fact that the exfoliation is successful with this range of electrical current, but is too slow and thus not optimal nor feasible. Fig. 6 shows the setup on day 7.

The electrical range of 0.2 - 0.3A yielded a significant volume of graphene at a good pace. Towards the end, the solution did not overspill. The graphene collected was significant. This amount was dried and sent for testing to investigate the quality. Fig. 7a shows the setup on day 5; Fig. 7b shows the setup on day 7. Fig. 9 shows the samples of graphene collected after drying in oven.

For electrical current ranges of 0.3 - 0.4A and >0.4A, the experiment was unsuccessful. It is conjectured that the current was too high, suggesting these electrical current ranges were too aggressive. In the first case, the solution overspilled on day 3. In the second case, the solution overspilled on the first day itself. Thus, the experiment could not go forward. Fig. 8 shows the effervescence seen with current 0.3 - 0.4A before overspilling.







Fig. 9: 0.2 - 0.3A Graphene sample after drying

H. Test Results and Analysis:

The tests conducted on the graphene sample are 'Raman Spectroscopy' and 'SEM/EDAX', to investigate the quality of the graphene yield. The tests were conducted only on samples from 0.2 - 0.3A, as the four other electrical current ranges either failed in quantity of graphene produced, or were unsuccessful.

H.1 Raman Spectroscopy

Raman Spectroscopy is a non-destructive chemical analysis technique which provides detailed information about chemical structure, phase and polymorphism, crystallinity and molecular interactions (*What Is Raman Spectroscopy? - HORIBA, n.d.*). It is based upon the interaction of light with the chemical bonds within a material. The process produces a Raman Spectra, which features peaks. Each of these peaks corresponds to a specific bond, for example C-C present in graphene.

Fig. 10 below shows the result of the Raman Spectra generated. The peaks at 1549.39 and 2981.05 confirm that the material formed is graphene. As indicated, the blue lines indicate carbon peaks, as shown by the key in the top right corner. The slight shift in the peak position may be due to the sulfur 'S' impurity.



Fig. 10: Raman Spectra

H.2 SEM/EDX:

Scanning Electron Microscopy (SEM) with Energy Dispersive X-Ray spectroscopy (EDX) is a surface analytical technique. Using a highly-focused, scanning (primary) electron beam, high resolution images of surface topography with high depth of field are produced (*Surface Science Western, 2022*). This image is constructed by measuring secondary electron intensity as a function of the position of the scanning primary electron beam. High spatial resolution is possible because the

primary electron beam can be focused to a very small spot (<10 nm). High sensitivity to topographic features on the outermost surface (< 5 nm) is achieved when using a primary electron beam with an energy of < 1 kV.

Fig. 11 below shows the results of the SEM/EDX test. Fig. 12 and Fig. 13 are two images produced using this technology. 'Spectrum 1' in Fig. 11 highlights the elements present, confirming the presence of the sulfur impurity in the carbon. The magnification in the images is not very high, and thus the single graphene layer is not explicitly visible. However, in Fig. 13, one of the visible graphene flakes has been labelled.





Graphene / Flake



Fig. 12: Image 1

Fig. 13: Image 2

I. Experimental Limitations:

As shown by the Raman Spectra and SEM/EDX results, there was the presence of sulfur as an impurity. This could be due to residue from the electrolyte, which was ammonium sulfate. This highlights the importance of the washing and purification of the graphene sample when collecting and drying it in the oven. In future studies, the graphene collected should be washed more thoroughly, or a greater number of times. A finer filter mesh could also be used instead.

Furthermore, the differences in current and voltage may have induced different rates of evaporation of the electrolyte during the process. While a lid was placed in this experiment, it did not 'seal' the system. In future studies, a suction lid should be used allowing for proper sealing on the beaker.

J. Conclusion:

Overall, graphene has proved itself to be an exceptional 'wonder material', having huge prospects for the future. It seems to play a pivotal role in the development of a range of industries. However, the manufacture of graphene is something that has large scope to improve in the future.

While many methods are available, Electrolytic Exfoliation is sustainable, simple and scalable, but lacks in quality. The study found that the optimal range of electrical current was 0.2 - 0.3A in a lab setting. In the future, this range could be further studied to get a more accurate electrical current value that yields the highest quality of graphene through this clean and green method.

The graphene synthesized was sent for testing and confirmed as graphene using Raman Spectroscopy and SEM/EDX. While there was a sulfur impurity, the problem can be overcome by washing the graphene collected a greater number of times.

Overall, the future of this novel nanomaterial is very bright. With more research into its manufacture and applications, graphene has the potential to change the world as we know it today.

K. Acknowledgements:

This study was carried out in an NABL approved laboratory 'Khanna Paint Testing Lab', where the DC setup and other necessary materials were available. This study was carried out under the guidance of Professor A.S. Khanna (Retd. IIT Bombay), Director of the laboratory.

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