Plasma-assisted Electrochemical Synthesis of Pristine Graphene Sheets

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Abstract

Graphene is a two-dimensional form of graphite made up of a single layer of carbon atoms in a honeycomb lattice that has attracted tremendous interest for its novel physical properties. A key challenge that has emerged is how to synthesize large amounts of graphene (large area or mass) at low cost. The objective of this project is to explore an entirely new method to exfoliate graphene from commercially available graphite products such as pyrolytic graphite (PG) or highly ordered thermal pyrolytic graphite (TPG). Our idea is based on electrochemical exfoliation where a current flows through an electrolyte to enhance the exfoliation of graphene flakes from graphite. A plasma is used as one of the electrodes to amplify the electric fields that are created in solution. In this paper, we present the new process and preliminary characterization of synthesized graphene material by Raman and UV-vis absorbance spectroscopy.
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Preface

This is a summary of several months worth of work as well as a couple months of preparation and reading prior to the start of actual experiments. I decided to do this project out of curiosity and a strong desire to learn more about Graphene. I had done some work with it prior to beginning on my project in my Quantum Mechanics class and when Professor Gao offered me the opportunity to work on the exfoliation process I agreed with hesitation.

If I could leave you with only one message, it would be to pick a research project you are extremely interested in. Research may seem overwhelming, time consuming and frustrating, but when you enjoy the work and can be pleased with whatever results you get, its not nearly as painful.
Acknowledgements

I am extremely grateful for all the help and guidance I received from a number of people while carrying out this project. Professor Gao has given me a number of opportunities to work on several different projects during my undergraduate work. He has provided guidance in a number of instances and has been a wonderful professor, mentor and advisor.

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I also owe quite a bit of thanks to Seung Lee. He was instrumental in the completion of my capstone. He provided much of the guidance I needed to carry out experiments and was a great resource when I was learning about Graphene exfoliation.

Lastly, I’d like to thank Professors Singer and Petchek for their guidance and advise throughout my capstone project.
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Section I

Introduction

1. Background

The term graphene was first coined in 1987 [1] by S. Mouras, to describe a single layer of graphite. Graphene consists of a single atomic layer of carbon atoms, making it a two-dimension lattice. The atoms are arranged in hexagonal structure creating a sheet of tightly bonded carbon. The synthesis of graphene, or few-layer graphene dates back a number of years. Transmission Electron Microscopy (TEM) images can be found as far back as 1948 [2]. Back then the field was not quite as popular as discoveries such as the electrical and mechanical properties of graphene had not been well documented yet. Instead the focus of single-layer carbon sheets focused on carbon nanotubes. Furthermore, up until then a good exfoliation process had not been developed, so studies of truly monolayer graphene were limited. Graphene
emerged as a desirable material in 2004 when Andre Geim and Konstantin Novoselov first exfoliated graphene flakes using the scotch tape method and made initial characterization tests [3]. Their method, while tedious and unreliable, allowed for the first monolayer graphene sheets to be exfoliated. Since then there has been a large increase in mono- for few-layer materials.

Upon the exfoliation of graphene, characterization of the electrical and mechanical properties took place, revealing the uniqueness and value of graphene. Along with the characterization of graphene, much work has gone into perfecting the exfoliation process, especially for uses outside of academic research.

2. Motivation

Graphene exhibits a number of unique properties: electrically, mechanically, optically and otherwise that make it a very desirable material for industrial use.

Electron transport measurements of graphene have shown it has high electron mobility at room temperature [4]. Combined with a good carrier density, graphene has a very high conductivity, greater than that of silver. These high quality electrical properties make graphene an ideal material to replace silicon for use in digital integrated circuits and transistors. Graphene has been used to create extremely small and extremely fast transistors, at one point the smallest transistors ever created [5]. Graphene transistors can now be cycled at 100 GHz, four times faster than the previous fastest graphene transistor, and almost twenty five times faster than current commercial transistors.
Graphene also exhibits excellent mechanical, thermal and optical properties. Its breaking strength is almost two hundred times greater than that of steel [6], and because it is lightweight it has several potential applications in construction and manufacturing. In addition, its flexibility, high conductivity and near complete transparency could improve upon current video displays in the touch-screen and liquid crystal display industries. [1] Other desirable traits of graphene include its large surface area to volume ratio, which plays a big role in capacitors and solar panels.

These traits make it an extremely versatile material, desirable in numerous industries at different sizes and quantities. However, most of these properties are highly dependent on the quality of the carbon lattice. If the lattice is bonded to a functional group -called a functionalized sheet of graphene- the material will not behave as desired. Many of the properties will change, most notably the transport properties. Thus, the conundrum of how to create large and clean sheets of graphene has been and area of intense interest.
3. Previous Work

In order to make graphene a viable material for industrial applications, a production method must be developed that synthesizes a high quality graphene product at a large scale. Moreover, it must be a relatively cheap and reliable method. Cost and reproducibility play a large role in this field. Various approaches have emerged in an attempt to create graphene sheets although most result in a low quality product, are not scalable or cost far too much for practical purposes.

My project focuses on combining an emerging technique, plasma-assisted electrochemistry with one of the established methods of exfoliating graphene, electrochemical exfoliation. To fully understand the uniqueness and originality of this approach, a strong understanding of the current status of the field is necessary.

a. Mechanical Exfoliation

Mechanical exfoliation was the first process to successfully exfoliate graphene for characterization purposes. The “scotch tape method” pioneered graphene exfoliation, and for their work Geim and Novoselov earned the Nobel Prize in Physics in 2010. The method is extremely simple, press a small amount of scotch tape onto a piece of graphite and slowly pull the tape away from the graphite sample. Because the bonds between the sheets are so weak, the tape pulls away the first atomic layer it’s adhered to. It is a very simple process and is very successful. The drawback is hours of exfoliating using several roles of tape to get only a few viable samples. Furthermore, do not expect to see factories of enormous roles of scotch tape attached to mammoth graphite samples. This process does not scale
well at all. Certainly there are some applications that could use graphene sheets of only a few centimeters, but for larger scale applications, this process simply does not translate to a viable exfoliation technique.

**b. Growth**

Growing graphene has also been explored at great lengths. If tearing apart graphite samples doesn’t work, perhaps piecing together graphite sheets can provide an easier and more reliable method. One such method is the annealing of silicon carbide [7]. By heating Silicon Carbide to temperatures in excess of 800 K, the silicon is evaporated away leaving behind a graphene sheet. This method can produce high quality sheets, but the environment required for growth is very delicate. Any contamination of the vacuum or variation in temperature can lead to a poor quality structure and there is still the extremely important issue of scalability. Maintaining a vacuum large enough for epitaxial growth would be difficult and in general the process is very expensive and impractical for industrial use.

An alternative technique for the creation of graphene sheets is chemical vapor deposition (CVD) [8]. This was one of the first ways of developing large-scale graphene sheets. The first sheets measured several square centimeters in area, much larger than previous yields of millimeters or smaller. The process involves dissolving carbon into a nickel substrate and then cooling the nickel, forcing the carbon atoms out via precipitation. By changing the cooling rate and density of carbon in the substrate, the thickness of the graphene thin film can be controlled.
The result of this process is large, high-quality graphene sheets. However, it is also a costly method of producing simple graphene sheets. For the emergence of graphene in industrial applications a cost effective method of exfoliation would be needed.

c. Electrochemical Exfoliation

Electrochemical exfoliation is another technique for exfoliating graphene. There are several variations of the technique, including the number of probes, currents used and chemicals used but the principles are largely the same.

The electrochemical cell is setup with a graphite anode and a metal cathode, such as platinum. Both probes are dipped into an electrolyte solution made of water and ionic liquid [10] or a surfactant [11]. Other chemicals can be added to enhance the conductivity of the electrolyte as well. The surfactant or ionic liquid intercalate the graphite anode, penetrating the layers of graphite. A voltage is applied across the probes, facilitating cleavage of graphene flakes at the anode. The electrolyte then stabilizes the graphene sheets in solution, preventing agglomeration after exfoliation.

Figure 3 An example of the intercalation and electrochemical exfoliation of graphene using an Ionic Liquid. This image courtesy of Jiong Lu [10].
These methods of exfoliating graphene have less control of the thickness, since multiple sheets could be cleaved at once, depending upon the success of the intercalation. However, these methods use readily accessible and “green” chemicals, which keep the cost of graphene synthesis down. An ideal technique would use inexpensive chemicals and provide a high yield of graphene sheets with adjustable properties based on the duration of the exfoliation, the amount of chemicals used, the temperature of the electrochemical cell or voltage across the probes. The graphene sheets exfoliated are small with largest ones being several micrometers per edge. The graphite anode is only a couple centimeters in area, thus putting a theoretical limit on the best possible yield. However, a new process of printing graphene sheets has emerged that makes use of graphene flake dispersions in water. Combining these techniques would make a scalable, cost effective method of generating high quality graphene sheets.
**d. Printing**

Printing graphene is a new technique that is extremely promising. The concept is extremely simple. It uses a well-established method of printing and change the ink. Felice Torrisi *et al.* developed a method of printing graphene structures, including transistors and transparent conductive patterns onto any substrate [12].

An inkjet printer uses graphene dispersed in a water solution as the ink for the printing process. The quality of the printed graphene component is dependent upon the quality of the graphene in the water dispersion. Thus, it essential to synthesize a high quality dispersion in order to fabricate a homogenous structure during the printing process. This means the graphene sheets must be single layer, un-functionalized and the structure must be defect free. The flakes must also not be too large as they may clog the nozzle. The target size for a sheet is one micrometer.
or less on each edge. Further requirements are placed on the graphene sheets as far as Reynolds, Weber and Ohnesorge numbers, however developing a tunable exfoliation method or re-suspending the graphene by using a filtration technique can account those for.

The ink is sent out via a 50-micrometer nozzle onto the substrate. Silicon Oxide is the typical substrate of choice although many other substrates can be used. During the printing process a “coffee ring” effect can occur preventing a homogenous film of graphene. In order to prevent this a solvent is used to maximize the wettability and promote adhesion. After the printing process is complete the entire wafer is heated for a brief amount of time to evaporate the solvent. What is left is uniform and homogenous sheet of pristine graphene, assuming the graphene ink is of good quality.

This report outlines efforts made to use an electrochemical exfoliation of graphene to create graphene dispersions adequate for graphene inkjet printing. Our exfoliation process would be tunable, scalable and exfoliate graphene sheets directly from a graphite source, ensuring maximum quality.
Section II

Exfoliating Graphene

This project was proposed with purpose of establishing a new technique for exfoliating graphene from a graphite source such as pyrolytic graphite (PG) or highly ordered thermal pyrolytic graphite (TPG). In developing a simple, efficient and cost-effective technique, we will enable a method of producing large sheets of high quality graphene when we combine our process with the graphene printing process described in Section I.3.d. This section outlines the method we developed and the results of our exfoliation.

I. Methods

Because graphite consists of weakly bonded graphene layers, we can use an electrochemical approach to remove the layers of graphene using a surfactant. We believe the surfactant will penetrate in between the layers of graphene and cleave layers of graphene off the graphite when a potential is placed across the electrochemical cell. This approach is very similar to previous attempts to exfoliate graphene, however our method uses a micro-plasma as the cathode rather than a traditional physical cathode, such as platinum.

We hypothesized this plasma-assisted exfoliation process would greatly improve upon previous efforts because the cathode would no longer cause the sheets to agglomerate on to a physical material, rendering the process ineffective. Instead, the graphene sheets would remain suspended in the electrolyte, stabilized
by the surfactant. The intercalation and stabilization of graphene with sodium dodecyl sulfate (SDS) surfactant is established by previous work [13]. We used a similar approach but replace the physical platinum cathode with our plasma cathode.

![Diagram](image)

**Figure 6** The intercalation of SDS is carried out through a two-step process. First oxidation for intercalation, then reduction for exfoliation. This figure is courtesy of Murat Alanyahonlu.

### a. Procedure

The procedure for creating the electrolyte with the SDS surfactant, and executing the exfoliation process is straightforward. The duration of the experiment depends upon the length of the exfoliation process, with minimal prep time. The plasma-assisted electrochemical cell method and setup was originally established to create colloidal metal nanoparticles [14], but we simply deploy it by using the graphite in place of the metal foil. Our setup is depicted in Figure 7.
The steps for preparing the electrolyte are outlined below:

1. Measure 80 milliliters of de-ionized water and place in beaker
2. Measure 0.8 grams of SDS, add to water
3. Measure 10.8 micro liters of 1M HCl, add to water and SDS
4. Stir for >10 minutes

The solution is then added to the cell, and the graphite cathode is dipped into the solution using a clamp. The clamp must not touch the water, as this could result in a disruption in the exfoliation process. The surface area of graphite in the electrolyte did not appear to hinder the exfoliation process. However, we ensured more than half of the graphite source was in solution during each trial. The plasma tip is lowered to just above the electrolyte. A thermometer is placed into the electrolyte and the whole cell is heated to 80°C. The entire experiment is done at atmospheric pressure in open air.
Argon gas is flowed through the plasma tip and the plasma is initiated by simply placing a voltage across the anode and cathode. The current is kept at a constant 5mA for the duration of the exfoliation process. Applying too large of a potential could oxidize the graphene.

The difficulty in maintaining a constant environment arises when the electrolyte begins to evaporate. This lowers the surface level of the electrolyte relative the plasma tip and lowers the voltage across the cell. This can be remedied by adding 1 mL of de-ionized water every 30 seconds to minute. Alternatively, the plasma tip can be lowered to maintain a consistent voltage. This process is rather grueling since it means the system must be closely monitored at all times. In the future, a system that feeds in water would benefit the process greatly as it would require less observation by the experimenter, and could provide more stabilized environment.

During our trials there were several difficulties in maintaining a good plasma. A satisfactory micro plasma is characterized by a purple color, arcing a distance of less than 1 cm. Any significant change in color or a complete loss of plasma will disrupt the exfoliation process. Bubbling can also occur from the argon or when de-ionized water is added to the cell. This created a problem when the bubbles came too close the plasma tip. If the bubble comes too close to the tip, the plasma is disrupted and the argon gas feeds directly into the bubble. This issue can be alleviated if water is added far away from the tip and if the tip is not lowered too close to the electrolyte.
Our process requires a significant amount of attention from the experimenter, however it is a large improvement over mechanical exfoliation methods. To enhance our exfoliation technique, we developed a filtering technique to remove any contaminates or unwanted carbon products that resulted from the exfoliation process.

To filter out the unwanted materials, we use a 0.025-micrometer nanopore filter and a vacuum pump. The filter is placed below a funnel and above a beaker that is connected to the vacuum pump. When the pump is on a vacuum created in the beaker sucks the solution in the funnel through the nanopore filter. The graphite material is collected on the filter paper, while unwanted material passes through into the beaker. 100mL of de-ionized water is also passed through the filter to wash off excess SDS still bonded to the graphene sheets.

The paper filter is then placed in a water solution and sonicated briefly to re-suspend the graphene sheets in a water solution. This method also allows us to measure the amount of graphene exfoliated. By measuring the weight of the filter paper before and after filtration, we can determine the total mass of exfoliated product. We can then control the concentration of graphene when it is re-suspended via sonication.

b. Results and Discussion

Following the exfoliation and filtration processes, we used various techniques to characterize our exfoliated product. These experiments will help the tuning process by determining what characteristics arise with various parameter
settings. It will also help optimize the process by determining the optimal chemical concentrations for exfoliation.

In this section, the characterization techniques and results are described. A visual examination, Raman Spectroscopy and UV-vis absorbance measurements were used and the outcomes are discussed.

i. Color Change

As mentioned in previous works [9][10][11] when graphene or other carbon materials such as nanoribbons or nanoparticles are exfoliated, there is an associated color change. For graphene sheets we first expect to see the colorless electrolyte turn yellow, then black over time. We may expect small black flakes in solution during while the solution is still yellow.

This method does not explicitly confirm graphene sheets, however it does determine the relative amount of exfoliated product. It is a simple first step towards determining whether the process is effective or not.

![Figure 8 A visual comparison of the final solutions. From left to right, De-ionized water, thermal exfoliation, electrochemical exfoliation with physical cathode, room temperature plasma-assisted exfoliation, and thermal plasma-assisted exfoliation.](image-url)
Initial results shown in Figure 8 reveal our technique greatly improves upon previous work. Most other techniques call for a 6-hour exfoliation process, however we accomplished a color change in less than 1 hour.

However, further experiments testing similar parameters did not have quite the color change as our initial experiments. We had quite a bit of difficulty reproducing some of our initial results. Despite this, our later results still show a distinct color change, still more significant than previous works.

These visual tests allow for a quick determination of a carbon based exfoliated product. As discussed in the previously mentioned references, it is also particularly useful for determining what stage the exfoliation process is in. For more a more quantitative analysis of the contents of our exfoliation solution we used Rama Spectroscopy and UV-vis absorbance.
ii. UV-vis absorbance

UV absorbance measures the amount of UV light a solution absorbs at a spectrum of wavelengths. To determine what material we have in solution, we use UV absorbance to indicate whether we have graphene sheets, nanoparticles or quantum dots or even graphene oxide. This technique is extremely important to determining whether or not our exfoliation process was successful. A high absorbance at the correct peak will indicate an abundance of graphene in solution. If other peaks are apparent, then our technique would need to be modified to exfoliate graphene rather than other carbon based materials. Moreover, this technique can compare the outcomes of different parameter settings in the exfoliation process.

Data on expected graphene UV absorbance results has been outlined in previous work [15]. Graphene is expected to have peak absorption at 270 nm. For our tests we used 3 mL of exfoliate solution and compared it to a base line of de-ionized water.

![Figure 10](image1.png) **Figure 10** UV absorption data based on different experiment durations. More graphene is exfoliated with increasing time.

![Figure 11](image2.png) **Figure 11** UV absorption data with varying SDS concentrations. Maximum exfoliation occurs near 10 mg/mL, more SDS simply saturates the solution.
The UV data leads us to some interesting conclusions concerning the contents of our exfoliation solutions. Figures 10, 11 and 12 show distinct peaks at 270 nm indicating there is a presence of graphene in our solutions. However, absorption continues to grow at shorter wavelengths. The primary peaks appear to line up with those suggested for graphene oxide near 230 nm [16]. Unfortunately, this indicates our solutions have a significant amount of graphene oxide. We used Raman Spectroscopy to further look at the contents of the exfoliated solution.

**iii. Raman Spectroscopy**

Here we used Raman Spectroscopy to further characterize and identify the contents of our exfoliated solution. Previous work suggests a G-band peak at 1300 cm\(^{-1}\) [17]. The presence of a large D band would indicate a non-graphene product, such as graphene oxide or possible carbon quantum dots.
The Raman data indicates the presence of graphene quantum dots [18], as indicated by the large D-band at 1600 cm⁻¹. This result combined with the UV absorption data suggests we are exfoliating materials other than pristine graphene sheets. Instead, we have both graphene oxide sheets and graphene quantum dots. It is possible that by using our filtration technique we could remove the quantum dots, however, both the Raman and UV results suggest that some graphene material has been exfoliated.

As mentioned before, the exfoliation process is a tunable process. It can be altered to give different results, and its possible that finding the correct concentrations of SDS, HCl and water as well as the right temperatures, durations and currents could still yield a better graphene dispersion.
c. Conclusions

We present a new method of exfoliating pristine graphene using a plasma-assisted electrochemical approach. Our technique expands upon previous techniques by using a micro-plasma as the cathode of the electrochemical cell instead of a physical cathode. The result is a decrease of agglomeration and greater exfoliation of carbon materials. We also describe an original method of filtering the resulting graphene solution using a nanopore filter.

Unfortunately our characterization tests indicated there was a large abundance of non-graphene carbon material exfoliated. The UV absorption data reveal primary peaks near 230 nm, indicating the presence of graphene oxide. The Raman data showed a large D-band indicating graphene quantum dots. The large concentration of these materials other than pristine graphene suggests our process is not optimized for graphene exfoliation. We will continue to pursue graphene exfoliation using Ionic Liquids for intercalation and stabilization during exfoliation.
References


