Synthesis of Graphene Fibers for use in Supercapacitors

by

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Author's Declaration

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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Abstract

Graphene a recently discovered form of carbon that has become an important material in the world of electrochemical storage due to a number of intriguing properties[1]. Graphene exists in many different forms in different dimensionalities such as graphene foams[2] and graphene paper[3]. However in the 1 dimension graphene has only been recently explored in the form of graphene fibers. Graphene fibers are a cost effective, mechanically flexible, highly shapeable fiber that employs the properties of graphene. Wet spinning can be used to synthesize graphene oxide (GO) fiber, which is later then converted in graphene fibers (rGO) via chemical reduction. This project found that using large flake graphene oxide of concentration greater than 8mg/mL, a syringe needle size of 150 μm, a pump rate of 0.5-1 mL/min, a coagulation bath of 5% NaOH/Methanol will produce robust graphene oxide fibers. Capacitance of graphene fiber can be as high as 2000 mF/cm^3. In order to further improve the strength of graphene fibers the wet spinning method was modified with a coaxial spinneret to add another polymer to coagulate along with graphene oxide. Chitosan was added to the coaxial spinneret to produce a chitosan-core graphene oxide fiber. It successfully produced long strands of chitosan-core graphene fibers up to about 1 meter in length. Chitosan core GFs were structurally improved compared to standalone graphene fiber, albeit it having a few discrepancies. The chitosan core was rendered a poor electrode for fiber-based supercapacitors.

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List of Abbreviations, Symbols and Nomenclature

GO – Graphene Oxide

GF – Graphene Fiber

rGO – reduced Graphene Oxide

HI – Hydrochloric Acid

CV- Cyclic Voltammetry

EDX – Energy Dispersive X-Ray Spectroscopy

SEM – Scanning Electron Microscopy

1.0 Introduction

1.1 Graphene

Graphene is identified as a flat monolayer of carbon atoms that are sp^2 hybridized. Its honeycomb network is the building block of many other carbon structures. Its structure allows for many dimensionalities from 3D to 0D. Graphene has been hailed as the “wonder” material due to its many distinguishing properties; extraordinary thermal, mechanical and electrical properties.[4]

1.1.1 History

It is important to note that graphene should be considered as the fewest layer limit of graphite. Graphite is a three dimensional structure comprised of stacked layers of 2D planes of carbon sheets (i.e. graphene). Graphite is abundant in supply and is a naturally occurring resource. It has been known as a mineral for about 500 years. Graphene on the other hand has always been assumed to not exist on its own until very recently. Landau and Peieris argued that strictly 2D crystals were thermodynamically unstable. Their theory argued that thermal fluctuations in such low dimensional lattices would lead to a displacement of atoms.[5]

The earliest attempts at synthesizing graphene were using chemical exfoliation. Bulk graphite is usually intercalated so that the layers of graphene within the graphite are separated by layers of interrupting molecules. This method resulted in two main problems. Firstly this resulted in different types of 3D materials. Secondly it becomes very difficult to get rid of intercalating molecules and often results in a sludge containing restacked graphene sheets. Due to its difficulty in control, chemical exfoliation has attracted limited interest.

Over the years many attempts have been made at graphene but research in the field was accelerated when Geim and co-workers at Manchester University successfully isolated single layer samples from graphite. Konstantin Novoselov and Andre Geim used scotch tape to clean the surfaces of graphite before performing analysis. They found that the scotch tape would mechanical cleave away layers of graphite to expose graphene. This led to an explosion of interest primarily due to the belief of that such 2D lattices were thermodynamically unstable. The single to few layer sheets of graphene flakes were attached to the scotch tape by only van der waals forces. When cleaved using silicon the graphene could be made free standing by etching away the substrate.[6]

Graphene can be seen as the mother of all carbon allotropes. As graphite can be viewed as the stacking of many layers of graphene, other structures can also be seen to be composed of some variation of graphene. Graphene can be rolled over to form carbon nanotubes as well as fullerenes (e.g. buckyballs).

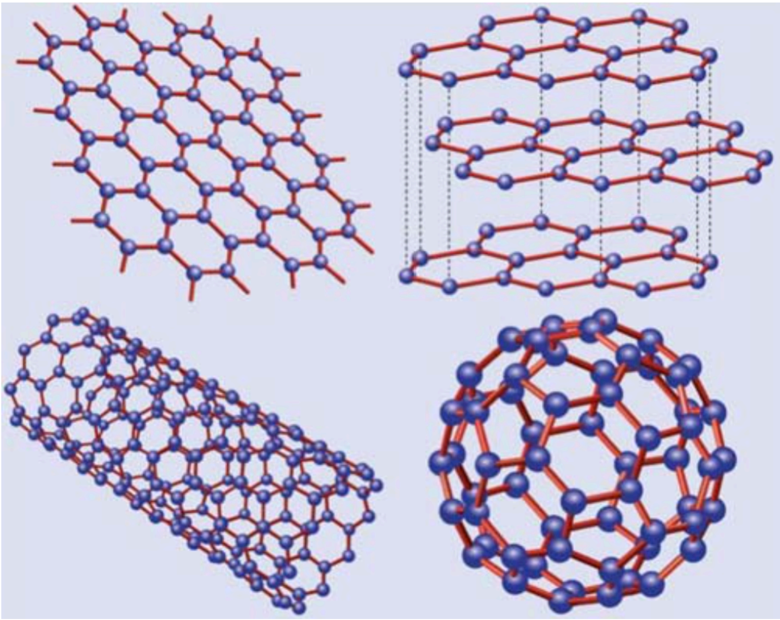


Figure 1 Different Carbon Structures [7]

Graphene has been viewed as the new age wonder material. By definition it's the thinnest known material in the world. It has zero effective mass and can travel for several micrometers without scattering at room temperature. Graphene is also known to have record thermal conductivity and stiffness values due to current densities six orders of magnitude higher than copper[8].

Since its conception in 2004 graphene has become the cornerstone for many research initiatives. This is due to it having many desirable properties that will make it an excellent material for many applications. Some of the many notable properties include:

- Room Temperature thermal conductivity (~5000 W m^{-1} K^{-1})
- Young Modulus (~1 TPa)

- Surface Area of 2630 m^2 g^{-1}[9]
    - Graphite: 10 m^2 g^{-1} , Carbon Nanotubes 1315 m^2 g^{-1}
- Conductivity ~ 64 mS cm^{-1}
    - 60 times SWCNT
- Electron Mobility ~ 200 000 cm^2 V^{-1} s^{-1}[10]
    - Silicon: 1000 cm^2 V^{-1} s^{-1}

Many of these properties were expected based on the study of carbon nanotubes, because as mentioned before graphene is the basic building black of many carbon dimensionalities such as carbon nanotubes. The reason these are higher are due to the absence of crystal and edge defects [8].

1.1.2 Graphene Synthesis

Mechanical Exfoliation

In 2004 when Konstantin Novoselov and Andre Geim discovered graphene on scotch tape, they used a form of mechanical cleavage. The idea behind obtaining graphene using this method is by using scotch tape to peel a layer off of highly oriented pyrolitic graphite and depositing onto a silicon substrate. Mechanical cleavage of graphene layers from graphite is the most facile and cost effective method in obtaining layers of graphene. It is also one of the best ways to study layers of graphene. However its simplicity is also the reason that its not suitable for large scale synthesis of single layer graphene[11].

Although chemical oxidation and subsequent exfoliation (explained in subsequent sections) provide an easier method to producing larger amounts of graphene, these methods are chemically invasive and generate many structural defects. These structural defects contribute to disrupted electronic structures of graphene. The chemical reduction methods used to return the oxidized graphene back to its original state such as thermal reduction make it virtually impossible to regenerate the original graphene structure [12]. This is where mechanical exfoliation presents a significant advantage, and thus is more favourable when it is a necessity to maintain the original graphene structure.

Chemical Vapor Deposition

Chemical vapor deposition is one of the best ways to produce defect free continuous layers of graphene due to its controllable parameters [13]. The nucleation and growth of graphene is controlled by the exposure of some transition metal surface to a particular hydrocarbon gas under low pressure. An example setup would be the exposition of polycrystalline Ni film at 900 °C to a diluted hydrocarbon flow under ambient pressure. This will result in a layer of ultrathin graphene film (about 1 to 10 layers) over the Ni surface. The nickel films are then electron beam evaporated onto silicon substrates and thermally annealed before the CVD synthesis.

It has been demonstrated that continuous films of graphene can be grown by ambient pressure CVD on polycrystalline Ni and transferred to a large variety of different substrates. These films demonstrate a comparable structure quality to existing graphene materials but are fabricated without the need of bulk single crystal substrates. The graphene film size is determined by the area of the Ni growth surface and is only limited by the CVD chamber [14]. Unlike the other methods of synthesizing graphene, CVD produces very uniform and defect free graphene layers. However since the Ni film area and the size of the CVD limit it, scalability is very limited and very expensive.

Chemical Exfoliation

One of the more popular methods in synthesizing graphene is through chemical exfoliation or sonication assisted exfoliation. It involves the exfoliation of graphite in organic solvents through the use of surfactant complexes. Graphite flakes are dispersed in surfactant solutions and then transformed into layers of graphene through ultrasound, which result in graphene-surfactant complexes. Through the use of centrifugation the graphene solution is separated, where the supernatant contains dispersion of graphene monolayers [15]. One example was the use of gum Arabic as an emulsifier to produce high yield graphene [16].

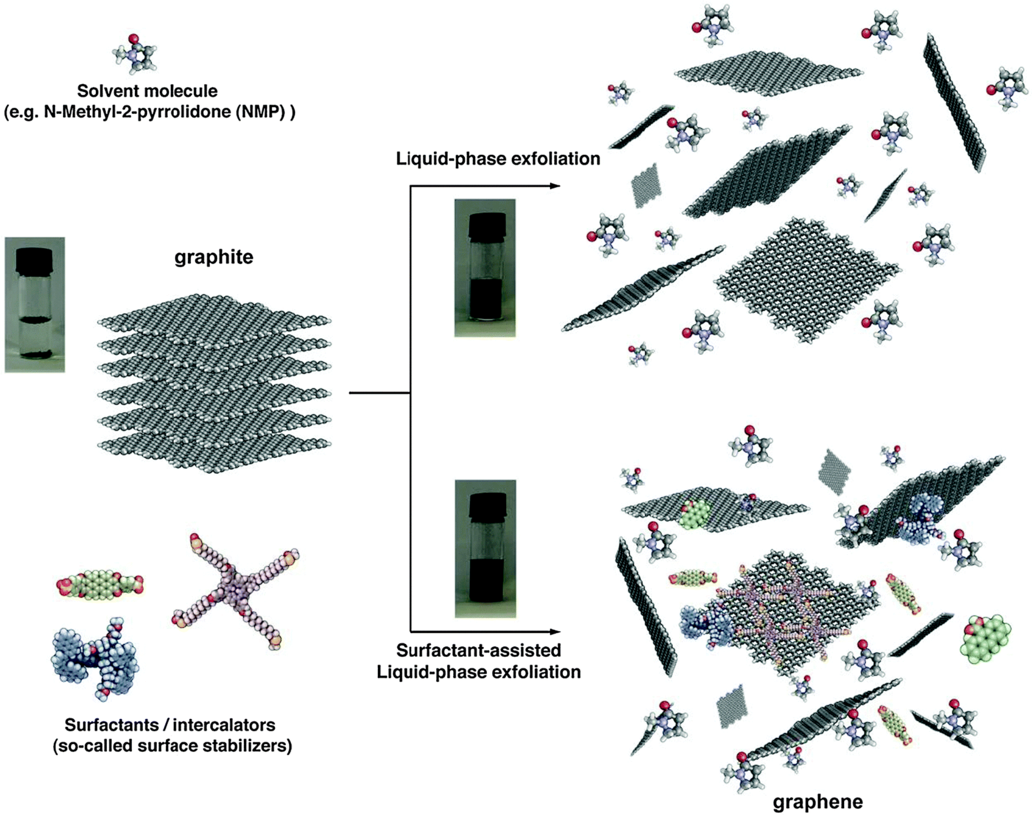


Figure 2 liquid-phase exfoliation process of graphite [9]

The advantages of this method are that it is very direct, simple and large-scale production is scalable. It also produces moderate yield and sample handling is very practical due to the graphene monolayers being suspended in liquid. However it is very time consuming which will result in high costs. The graphene dispersion can also be contaminated from the surfactants and solvents used.

1.2 Graphene Oxide

The mentioned methods are all good routes for device assembly and smaller scale synthesis of graphene. However they are less effective for large-scale manufacturing. The number one obstacle in synthesizing few layer graphene is the interlayer van der Waals forces between the graphene [17]. To date the best and most effective way of large scale manufacturing of graphene is through the Graphene oxide route, which involves functionalizing the layers of graphite with oxygen groups and separating them in graphene oxide sheets, which are then dispersible in an aqueous solution.

Graphene oxide is another method of chemical exfoliation, in which strong oxidizing agents are introduced into graphite. The exact structure of graphene oxide is difficult to determine, however it can be determined that the aromatic lattice of graphene is now modified with the presence of alcohols, ketone carbonyls, epoxides and carboxylic groups [18].

The synthesis of graphene oxides has undergone several iterations in development starting in 1859 where Brodie first synthesized GO by adding potassium chlorate to slurry of graphite in fuming nitric acid. In 1898 Stuadenmaier used sulfuric acid along with the nitric acid to improve on this protocol. This resulted in highly oxidized GO in a single reaction vessel, which made this method more applicable to large-scale synthesis. In 1958 Hummers further improved this method by treating it with Potassium Permanganate ($KMnO_4$) and Sodium Nitrate ($NaNO_3$) in concentrated sulphuric acid. This is the most common method that is still used today, albeit with some modifications.

Once graphene oxide is synthesized, it can be used to implement in many different applications to produce structures such as graphene oxide foams, graphene oxide films and graphene oxide fibers. In order to change these graphene oxide structures back to graphene structures, a form of reduction needs to be applied. There are three major ways to reduced graphene oxide back to graphene.

1.2.1 Chemical Reduction

When dispersed in solution, there are a variety of ways to chemically reduce graphene oxides back into graphene. The most commonly used is hydrazine monohydrate. Unlike other strong reducing agents, hydrazine monohydrate does not react with water, which makes it an excellent option for reducing aqueous dispersions of GO. Other reducing agents used include Ascorbic Acid, Sodium Borohydride, Hydroioidic Acid. Although it is not known how hydrazine reacts with graphene oxide, the reducing agent has been studied and a proposed pathway for its reduction can be seen in figure 3 below.

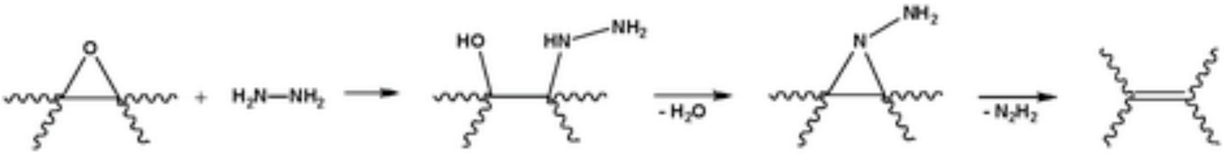


Figure 3 Proposed pathway for Hydrazine Reduction [11]

One of the biggest disadvantages in using chemical methods of reduction such as hydrazine is the presence of heteroatomic impurities. When oxygen functional groups are removed, nitrogen from hydrazine remains covalently bonded to the surface of graphene oxide in the form of amines or other similar structures. This results in a non-pristine form of graphene, however it has a positive effect on the electronic performance functioning as n-type dopants.

1.2.2 Thermal Reduction

Chemical reduction is the most popular method of reducing graphene oxide, but it isn’t the only method. Thermal exfoliation and reduction of GO is also effective and many studies have been done on said results. The idea behind thermal reduction is to strip the oxide functionality from the surface by directly heating GO in a furnace [19]. A notable effect of thermal reduction is the structural damage caused by the release of carbon dioxide. Also to note is that it is expected about 30% of the mass of the GO is lost during the exfoliation process resulting in vacancies and defects through the planes of the reduced graphene. These defects can affect the electronic properties of the product.

1.2.3 Electrochemical Reduction

The final method that is worth noting is the reduction of graphene oxide through the electrochemical removal of the oxygen functionalities. The advantage of this method is that the use of dangerous reducing agents can be avoided and there will no need to dispose of any byproducts. Electrochemical reduction is usually done on a variety of substrates that have graphene oxide deposited on (i.e. film). Electrodes are placed at the opposite ends of the film and linear sweep voltammetry is run using a potentiostat [20]. This method is very effective at reducing oxide functionality, however scalability is limited to the size of potentiostat capabilities.

1.3 Graphene Fiber

Graphene exists in many forms. Over the many years since its conception in 2004 many different types of graphene structures have been extensively studied and explored. In the 3- dimensionality there are structures such as graphene aerogels, which possess unique properties useful to many industrial applications such as seawater desalination, thermal or acoustic insulators, solar energy collectors, catalyst support and electrodes for supercapacitors and batteries. Graphene aerogels are electrically conductive with very high surface area. In the 2 – dimensionality there exists graphene paper, which a highly ordered sheet of graphene usually created by a byflow-induced assembly of graphene oxide sheets dispersed in a solution. It has excellent mechanical strength, thermal stability, high electrical conductivity, and biocompatibility, which make it a promised material for many biomedical applications. With all these different structures existing in different dimensionalities, there are almost no structures for graphene in the 1- dimensionality. This brings us to the recent phenomenon of graphene fibers.

3D GRAPHENE AEROGEL **2D** GRAPHENE PAPER **1D** GRAPHENE FIBER

Figure 4 Various Structures of Graphene

There are several carbon-based fibers that have been explored in research. The most prominent being carbon fibers, used in daily life because of its lightweight and high strength property. Carbon nanotube fibers are also a significant discovery, due to its high strength and high electrical conductivity [21]. However CNT fibers are very expensive to assemble and require very high temperatures and dangerous chemicals such as sulfuric acid. Graphene being the most recent phenomenon in carbon-based materials is the next ideal candidate for a fiber based structure. High electron mobility, high thermal conductivity and elasticity would be ideal in a fiber. To date several research groups have successfully assembled graphene into macroscopic fibers. This has opened up more avenues for research due to the lower cost of synthesizing GFs compared to CNTs and commercial carbon fibers, and as well the possibility of a plethora of new applications [22]. Graphene fibers can be used in many different applications such as smart clothing and textiles, flexible cable or fiber type electrochemical devices such as batteries and supercapacitors.

1.3.1 Graphene Fiber Synthesis Methods

There are several methods to successfully fabricating graphene fiber. The more successful ones are identified below.

Hydrothermal Strategy

It has been shown that hydrothermal treatment of GO will result in spontaneous assembly of graphene sheets via the π – π stacking between the graphene layers. A group successfully developed a one step dimension confined hydrothermal strategy. Using a glass pipeline of about 0.4 mm in inner diameter. GO suspension was injected into the glass pipeline and baked at 230 °C for 2 hours after sealing the two ends of the pipeline. This resulted in the formation of a graphene fiber that matched the pipe geometry. The length and the diameter of the graphene fiber can be controlled by using a longer pipeline with vary diameter sizes. This method is also effective in integrating functional components into the fibers that will facilitate various applications such as electrochemical devices. As an example, magnetic nanoparticles were introduced into the GO suspension before baking. This resulted in a magnetic graphene fiber composite possess good mechanical flexibility and a good magnetic response [23].

Chemical Vapor Deposition

Zhu et al developed a method to creating graphene fibers from CVD grown graphene films. After using CVD to synthesize graphene films, the films are transferred from the growth substrate to an organic solvent. Upon drawing out the film from the solvent a fiber like structure is formed upon the evaporation of organic solvent. The surface tension and the evaporation rate of the solvent have very important roles in the formation of the graphene fibers. The same group also used CVD to directly grow graphene onto copper meshes. After removing the copper wires using an FeCl3/HCL solution, a network of hollow GF's was achieved [24]. This method is simple as it requires no additional setup and no reducing agent. The disadvantage is that this method is limited to the size of the CVD film.

Spontaneous Reduction

Hollow graphene fibers can be spontaneously formed on Cu wires based on substrate assisted reduction and assembly of GO. Using the approach, the metal substrates (Cu in this case) are oxidized to metal ions with the loss of electron, while accepting electrons reduces the graphene oxide deposited [25]. The electron transport through the metal to the GO allows for various 3D assembly of reduced Graphene oxide depending on the shape of the metal substrate. This method is advantages for structure-defined assembly of graphene [13].

Wet Spinning

Wet spinning is an old method that accounts for a significant fraction of the production of today's man-made fibers. The basic process involved a very viscous polymer solution to be extruded through a spinneret (small holes in a needle) which itself is immersed in a liquid bath. The polymer is solidified in a fiber from the diffusional interchange that takes place between the fluid filaments. This process is known as coagulation, and the bath the spinneret is immersed in is called the coagulation bath. During coagulation the bath components diffuses into the filament, while the solvent diffuses out of it. This exchange causes the polymer to precipitate. It is insoluble by chemical reaction of the polymer or by an excessive buildup of nonsolvent or by both[26].

Zhen xu et al discovered the graphene oxide sheets in certain concentrations can form a chiral liquid crystal in their aqueous dispersion. This dispersion obeys a twist-grain-boundary phase model. These properties make Graphene Oxide a wet spinnable solution to produce graphene oxide fibers. It is important to note that not any size graphene oxide sheets in the dispersion will make the GO a liquid crystal. The average lateral width used by Zhen xu et al is 0.81 um with an average thickness of 0.8nm [27].

1.4 Supercapacitors

An electric capacitor has a sandwich structure that contains two conductive metal plates separated by a dielectric or insulating material. When a voltage difference is applied across the two plates, the positive charges accumulate on one plate while the negative charges accumulate on the other plate. When the voltage is removed, the charges remain at their corresponding electrodes. This is how the capacitor stores energy. If these electrodes are then connected using a conductive wire, a discharging process occurs and the positive and negative charges will eventually combine in the conductive wire[28].

Capacitors that store energy through an electrochemical double layer at the electrode/electrolyte interface are colloquially known as supercapacitors or double-layer capacitors. “Electrochemical double-layer capacitor” is the name that describes the functionality of these devices. Supercapacitors have existed for many years, dating back to 1957. In 1969 SOHIO attempted to market such devices. However not until the 90’s did supercapacitors become famous due to hybrid vehicles. The supercapacitor was used to boost the battery or the fuel cell in the hybrid electric vehicle to provide the necessary power for acceleration and to recuperate energy from braking. Today many high tech companies continue to invest in the research and development of supercapacitors primarily to boost component supporting batteries or to replace batteries entirely[29].

Supercapacitors compared with conventional metal capacitors mentioned before have significantly higher specific energy. Supercapacitors have higher specific power than most batteries, but the specific energy is lower. A combination of high power capability and good specific energy, allows supercapacitors to position itself between batteries and conventional capacitors as seen in the ragone plot in figure 5. Batteries and fuel cells are usually lower power devices whereas conventional capacitors have a power density of greater than 10^6 watts. As mentioned before supercapacitors are often combined with existing energy systems; either to improve energy density or power density[30].

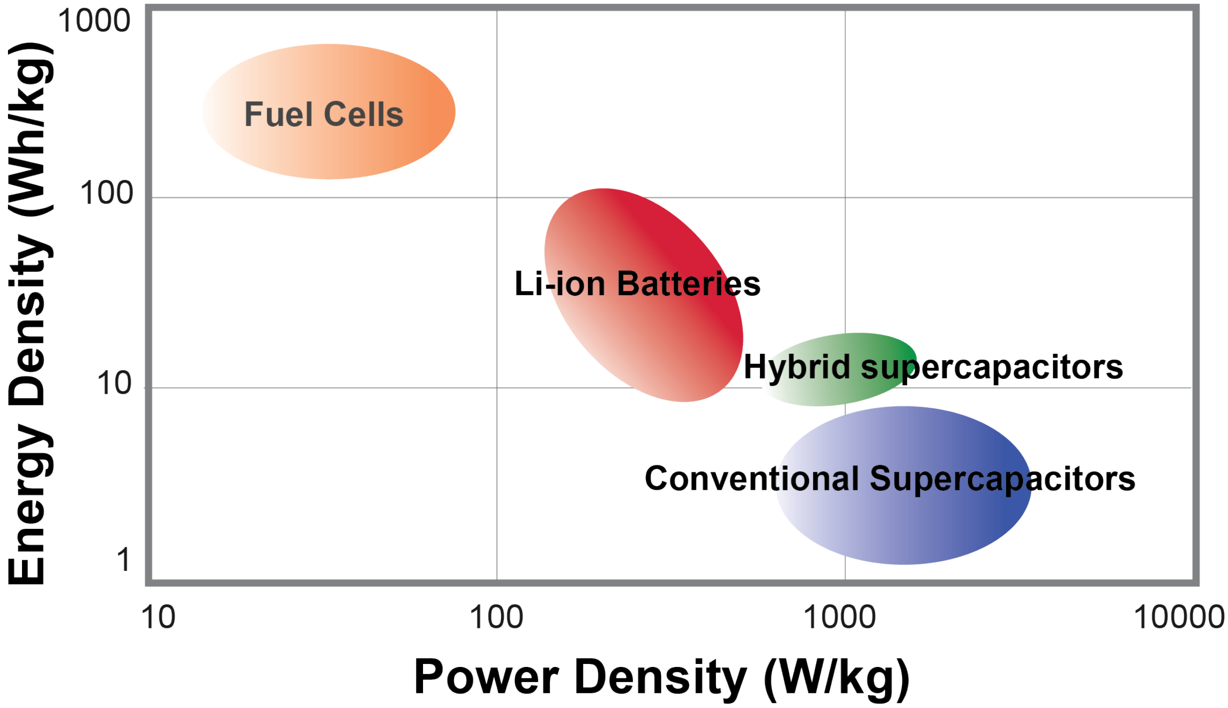


Figure 5 Ragone Plot

The concept of the supercapacitor is based on the electric double-layer existing at the interface between a conductor and the electrolyte solution. The electric double-layer theory was first proposed by Hermann von Helmholtz and further developed by other scientists such as Guoy, Chapman, Grahame, and Stern. The supercapacitor consists of two electrodes with an electrolyte between them (electrolyte is in the form of a solid or solution). In the solid-state electrolyte supercapacitor, the electrolyte plays the role of a separator and to conduct ions. In the liquid electrolyte supercapacitor, there is a requirement for a porous separator sheet that allows the ions to pass through, creating a conducting current. Figure 6 below shows the structure of a typical supercapacitor. On the positive electrode there is an accumulation of positive charges, which attracts an equal number of negative charges around the electrode in the electrolyte due to columbic forces.

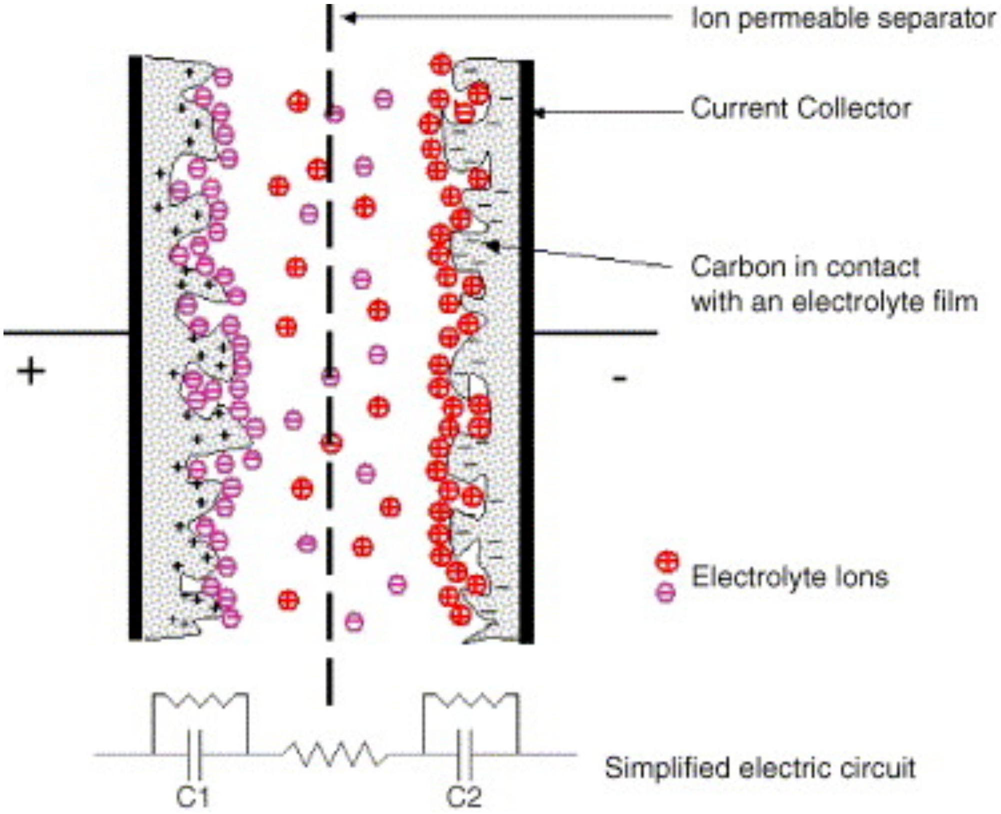


Figure 6 Structure of a supercapacitor [20]

The charge balance between the electrode and electrolyte represents an electric double layer. To maintain neutrality an equal number of negative charges accumulate at the opposing electrode which in turned induces a number of positive charges in the electrolyte. This forms another double layer. Thus a supercapacitor has two electric double layers, one at the positive electrode and another at the negative electrode.

1.5 Flexible Supercapacitors

With a lot of research and development being pushed towards the improvement of supercapacitors, a new branch of specialization has recently spawned to accommodate recent technological trends: flexible devices. Flexible power sources that are versatile and integrate with electronic devices of various size and shapes has been garnering a lot of attention. Being flexible and versatile allows these energy sources to be integrated into items beyond electronics such as wearable electronics [31].

Carbon based materials like graphene, carbon nanotubes, and activated carbon have attracted considerable interest in the development of flexible supercapacitors. A few examples that are being pursued right now:

- Nanoporous cellulose papers embedded with CNT electrodes and ionic liquid electrolytes [32].
- Coating of CNT on commercially available plain paper, which enables it to be highly conductive paper [33]

- Flexible fiber supercapacitor, which is made up of two fiber electrodes, a helical spacer wire, and an electrolyte. This led to a good electrochemical capacitance performance[31].

By studying graphene fibers, all these flexible electrochemical devices such as flexible supercapacitors can be further enhanced by offering the beneficial characteristics of graphene in a flexible fiber form.

2.0 Structural & Electrochemical Characterization Techniques

Characterization is very important for understanding and improving the results of our research. Characterization techniques can provide an understanding of the mechanism of how a nanomaterial is made, and provide the necessary guidance to further improve our research. This section outlines the characterization techniques used and how they work.

2.1 Scanning Electron Microscopy

The Scanning electron microscope is one of the most popular instruments available for the analysis of micro and nanostructure morphology and chemical compositions of materials. Figure 7 below shows the basic setup of a SEM. Image formation in the SEM is dependent on the signals produced from the electron beam and interaction in the sample. These interactions are divided into two major categories: elastic and inelastic interactions. Using an electron beam, electrons are targeted at the sample. Elastic scattering results from the deflection of the incident electron. Incident electrons that are elastically scattered more than 90 degrees are called backscattered electrons and are useful for imaging the sample. Inelastic scattering occurs in many different numbers of interactions and results in the primary electron transferring energy to that atom. The amount of energy loss depends on when the electrons in the sample are excited collectively and on the biding energy. The excitation of the sample electrons leads the generation of secondary electrons (SE) which can be used to analyze and image the sample[34].

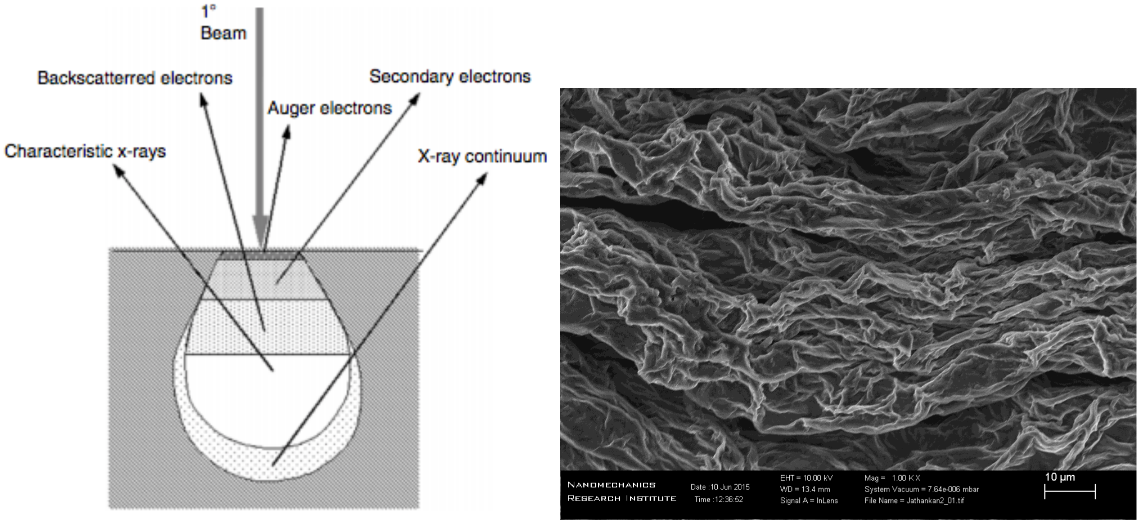


Figure 7 Setup of SEM and SEM image [34]

The rightmost image in Figure 7 is an example of an SEM analyzed image of graphene fiber.

2.1.1 Energy Dispersive X-Ray Spectroscopy

The backscattered electron mentioned above also display compositional contrast in the image that resulted from different atomic number elements and their distribution. Energy Dispersive Spectroscopy allows us to identify those particular elements and their relative compositions. The initial EDS or EDX analysis involves the generation of an xray spectrum from the scan area of the SEM. A sample EDX analysis chart is shown below. EDX analysis can be done with many modern SEM machines as the EDX detector is now included as a part of the setup[28].

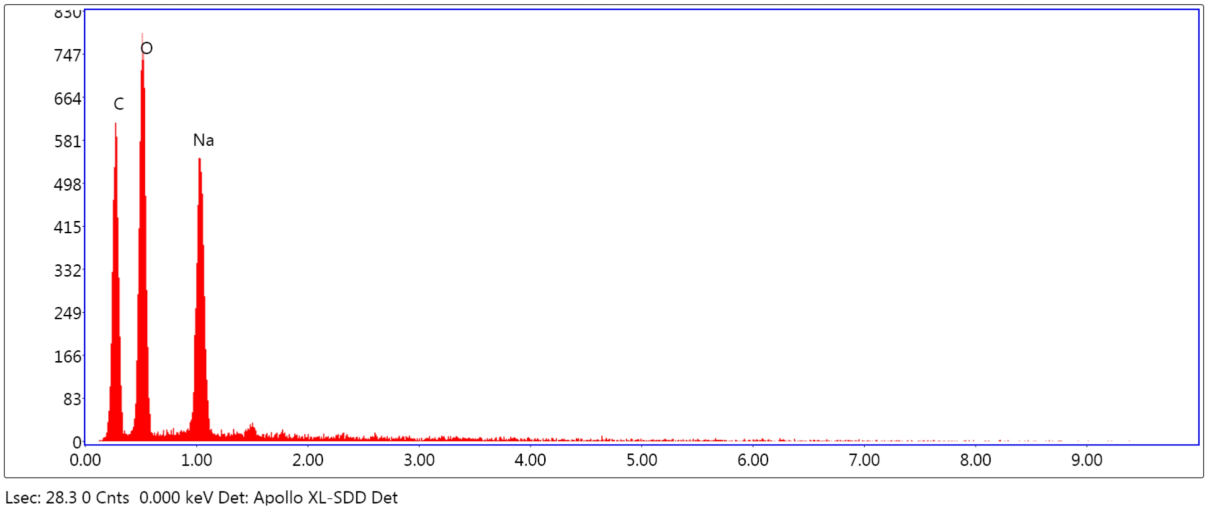


Figure 8 EDX chart example

2.2 Raman Spectroscopy

Raman spectroscopy involves the use of directing a layer at a sample and measuring the unique vibrational and rotational level structure. Raman scattering is the inelastic scattering of a photon, when a small fraction of scattered light is scattered by excitation, which leads to scattered photons with a different frequency than the incident photo. There are two types of scattering: Stokes scattering (molecule absorbs energy) and anti-stokes scattering (the molecule loses energy). The energy levels are unique for every molecule and the scattered light frequency is based on the structural characteristics of the chemical bonds. Thus the raman spectra is very specific, which makes it an important analytical tool in many research areas.

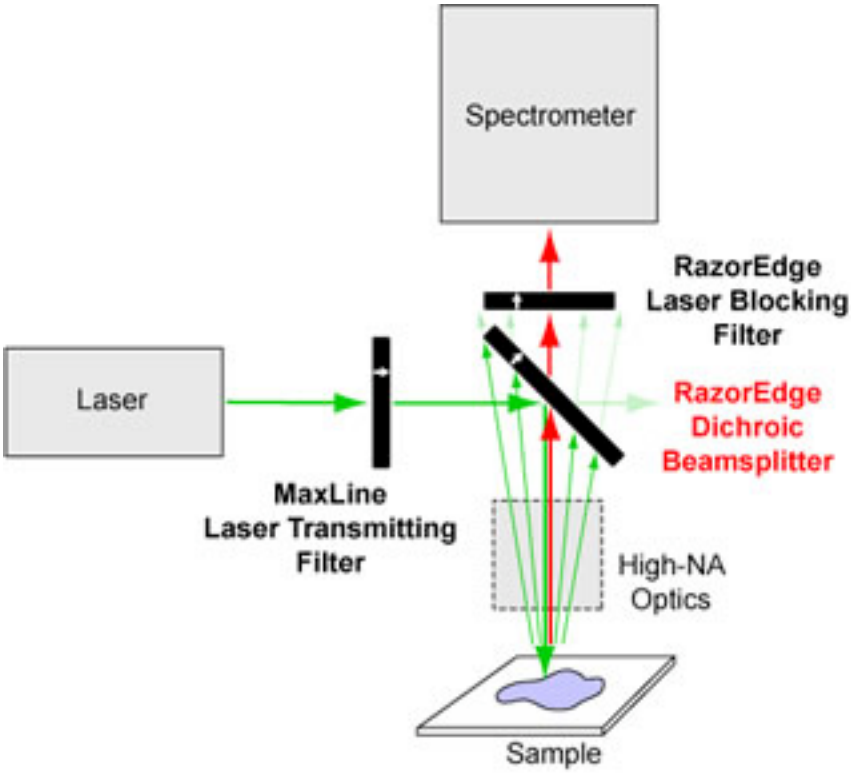


Figure 9 Raman Spectroscopy

2.3 Cyclic Voltammetry

Cyclic voltammetry (CV) is a potential-dynamic electrochemical technique. It is used obtain data about surface and solution electrochemical reactions including kinetics, reaction reversibility and others. Usually a potentiostat instrument is used to control the electrode potential. The CV analysis is usually done on a three-electrode configuration (half cell test), which contains the following: a working electrode, a counter electrode, and a reference electrode. CV analysis can also be done on a two-electrode test cell.

During the CV analysis, the potential of the working electrode is measured against the reference electrode via linear scanning between the upper and lower potential limits (which is set by the user). During the scanning of the electrode potential, the current passing between the working electrode and the counter electrode can be recorded. This is plotted to produce a CV curve like the one shown in figure 10. Using the following equation the specific capacitance of a double layer supercapacitor can be obtained.

$$C_s = \frac{\int i\, dV}{2\ x\ m\ x\ \Delta V\ x\ S'}$$

Cs is the specific capacitance, $\int i\, dV$is the integrated area of the CV curve, m is the mass of the active material, ΔV is the potential range, and S is the scan rate[35].

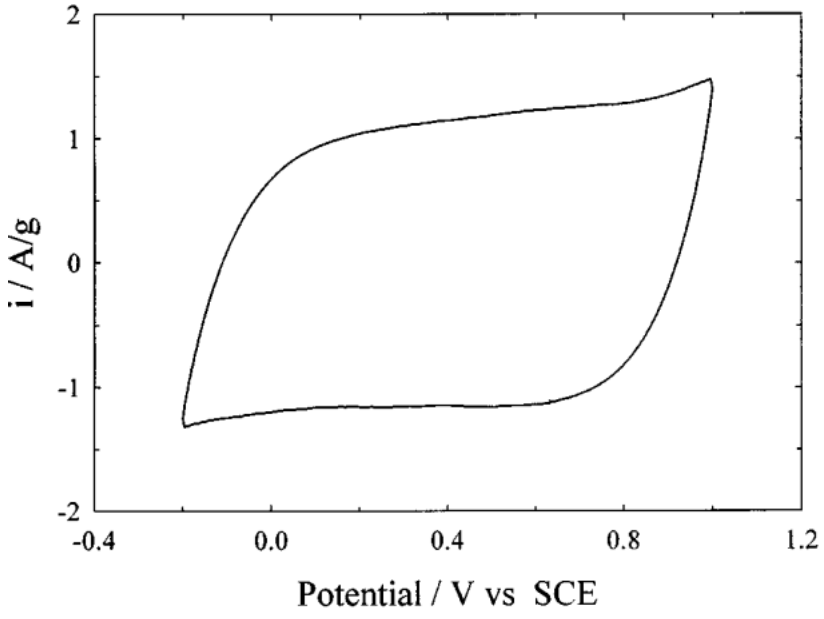


Figure 10 CV curve of supercapacative materials [36]

3.0 Graphene Fiber and supercapacitor performance

3.1 Introduction and Purpose of Study

As mentioned before graphene since its discovery in 2004 has become the forefront of many research initiatives due to its phenomenal properties. Many form factors of graphene have been established in the past few years such as graphene foams, films, and many different composites. The most recent phenomenon is graphene in its 1 dimensional form of graphene fiber. It introduces mechanical flexibility, high resistance to torsion, low cost, lightweight shape ability to an already feature rich graphene material[27]. With the world slowly moving towards flexible textiles and energy storage it is important to investigate the use of graphene fibers for electrochemical storage, in particular the supercapacitor.

In this study I focus on two very important goals; 1) to fabricate graphene fiber by wet spinning graphene oxide solution and 2) to test the supercapacitor performance of the graphene fiber. The study involves wet spinning large flake graphene oxide solution in a coagulant bath, reducing the graphene oxide fibers into graphene fibers, and finally testing capacitance of the fiber using a half cell/full cell test.

3.2 Experimental Methods

3.2.1 Graphene Oxide

The first step to wet spinning graphene fibers is to synthesize large flake graphene oxide, which compared smaller flakes has a significantly larger size of graphene oxide sheets. As mentioned before large flake graphene oxide solution portrays liquid crystal properties[27] and thus makes it an excellent wet spinnable solution. In this experiment a form of the modified hummers method was used to synthesis large flake graphene [17].

Graphene Nanoplatelets was purchased from XG Sciences with an average sheet size of 200 µm. These nanoplatelets are graphite pieces that have been exfoliated and thermally expanded already. 2 grams of graphene nanoplatelets and 1 g of Sodium nitrate ($NaNO_3$) were measured and put in a round bottom flask. 150 ml of concentrated Sulphuric Acid (H_2SO_4) was slowly added to the flask while stirring at 0°C (flask is in an ice bath). 6 grams of potassium permanganate ($KMnO_4$) was added a bit at a time, while the temperature of the reaction was kept below 10°C. After the potassium permanganate was completely added, the ice bath was immediately removed. The solution was then stirred continuously for 3 hours. 150 mL of DDI water was added to the solution, and stirred for another 30 minutes. 280 mL of warm DDI water and 40mL 30% H2O2 was used to dilute the solution further. The solution was then vacuum filtered and washed with 3 litres of 5% hydrochloric acid (HCl). The solution was vacuum filtered again with a metal mesh to remove unreacted graphite pieces. The cake after filtration was mixed with water and added to centrifuge tubes. Solution was continuously washed with water using centrifugation until the pH was 6. After washing the solution was collected into a bottle. By freeze-drying small samples of the solution the concentration was obtained.

3.2.2 Wet Spinning

In our lab there isn't an industrial size wet spinning machine so I put together a custom wet spinning machine. A typical wet spinning machine consists of the following components: motor, roller and a pump to push the solution through the needle. The diagram below shows the basic setup of wet spinning machine.

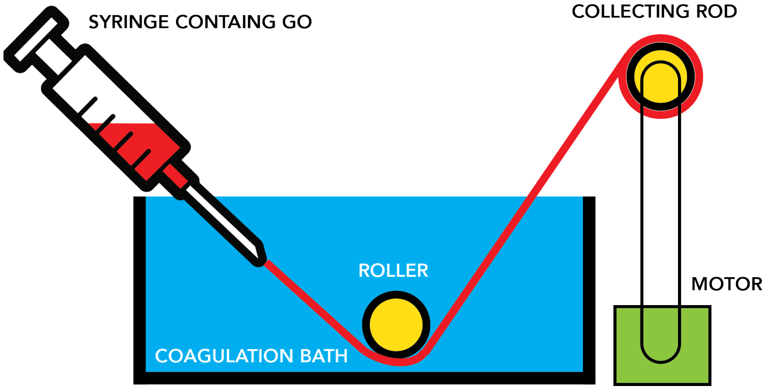


Figure 11 Basic wet spinning setup

Using a syringe pump, medical syringe and needles, beakers a wet spinning rig was put together. Using an arduino microcontroller a Teflon roller setup was also made to draw the fibers out of the bath and collect them. The arduino microcontroller can be used to control the speed of the Teflon roller, ultimately controlling the diameter of the spun fibres. Figure 12 below shows the wet spinning setup that was created in the lab.

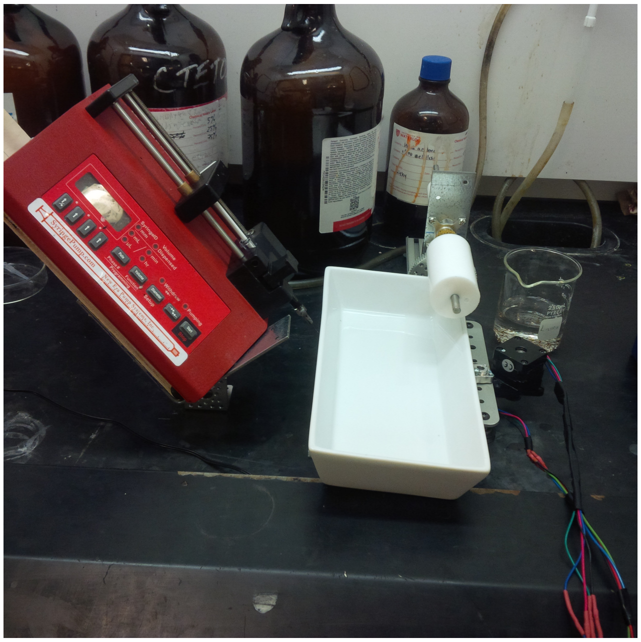


Figure 12 Custom wet spinning rig

The solution is put into the syringe, and pumped through a needle into the coagulant bath. The fibers are then extracted out of the bath, and air-dried for some time. This produces graphene oxide fibers, which will then be reduced in graphene fibers after reduction.

3.2.3 Parameter Control

The most critical aspect of this experiment is parameter control. Everything from the quality and size of the spun fibers can be optimized and fine tuned by adjusting various parameters throughout the experiment. The parameters have been in summarized in table 1 below.

Table 1 Parameter Control

Parameter	Description
Large Flake Graphene Oxide	Large flake fibers are crucial for the GO

	solution to exhibit liquid crystal properties.
Concentration	The concentration of the graphene oxide solution can affect the spinnability of the fibers. Too low of a concentration will result in failed fibers.
Needle diameter	The diameter of needle will contribute to the size of the fiber. Smaller the needle diameter, the smaller the fiber diameter will be.
Spinning Rate	This is the rate at which the solution is extruded through the needle into the coagulation bath. Too high or too low of a speed will result in failed fiber structures.
Collecting Rate	This is the rate at which the fiber is collected out of the bath.
Draw Ratio	This is the ratio between the spinning rate and the collecting rate. A ratio either too high or too low will result in curled fibers or structurally weak.
Coagulant Bath	The type of bath that is used for the GO solution to coagulate into fiber filaments is important in determining the final structure
Reduction	The type of reduction method used in reducing the graphene oxide fibers into graphene fibers is also important in obtaining strong fibers that are good for electrochemical activities.

3.2.4 Reduction

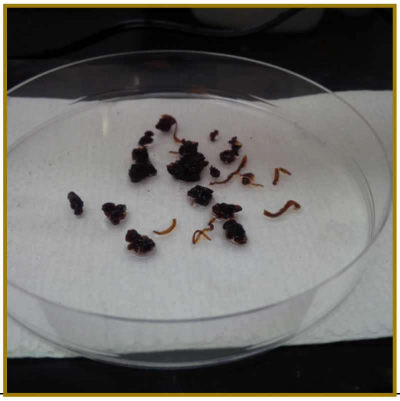
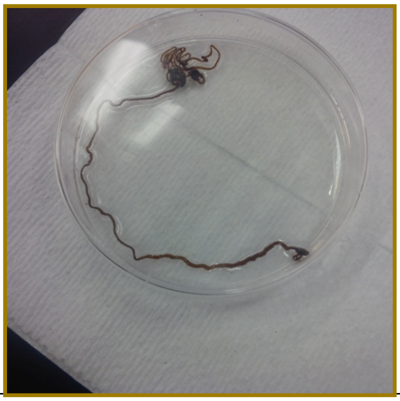
The fibers that are pulled out of the coagulant bath are graphene oxide fibers. Although high in strength and easy to handle with your hand, they are poor conductors and need to be reduced back into graphene fibers to be of any good use in supercapacitors. Graphene oxide has a variety of functional groups such as epoxyl, carboxyl and hydroxyl groups, and in order to become graphene these function groups need to be eliminated. The most common methods to deoxygenating GO involve high thermal annealing or low temperature chemical reduction. Since we are interested in keeping the structure integrity of graphene oxide fibers even after reduction, chemical reduction is more beneficiary method for graphene fibers. I used two major methods to chemically reduce the GO. The first one using hydrazine vapours and the second method is using hydroiodic acid. For hydrazine vapor, 2 ml of hydrazine solution (35%) is put in a beaker. A metal mesh is then placed over the jar where enough of the mesh is sinking in. The graphene oxide fibers are then placed over the metal mesh and sealed. The glass is heated to 80°C for 6 hours. Hydrazine vapors are formed throughout the beaker, which effectively reduces the graphene oxide fibers. For the second method, the fibers are places in a beaker with 15 ml HI acid (40%) and heated in a convection oven for 12 hours. After reduction the fibers are washed and dried. The fibers are then ready for electrochemical analysis.

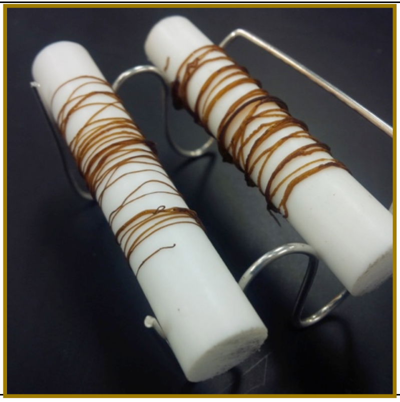
3.3 Results and Discussion

3.3.1 Optimal Parameters

In order to produce the best quality graphene fibers with good conductivity and high strength many trials were completed to optimize the best conditions and parameters. Table 2 summarizes the trials that occurred before finalizing the optimal set of parameters for the best fibers.

Table 2 Parameter Trials

Parameters	Graphene Oxide Fiber Quality
CONC : 2.45 mg/ml RATE: 5ml/h NEEDLE: 0.91mm NaOH/Methanol	
CONC : 6.15 mg/ml RATE: 20ml/h NEEDLE: 0.91mm NaOH/Methanol	
CONC : 6.565 mg/ml RATE: 10ml/h NEEDLE: 0.91mm Ethyl Acetate	

CONC : 6.565 mg/ml RATE: 20ml/h NEEDLE: 0.51mm NaOH/Methanol/H_2O	

After the many trials a set of optimal parameters was finalized. The optimal parameters are summarized in figure 13 below.

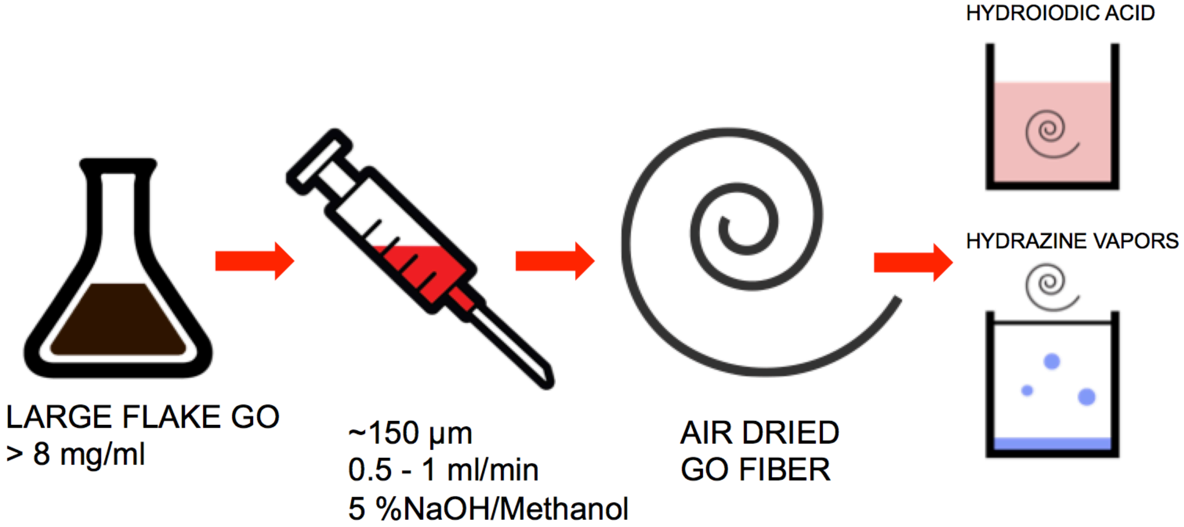


Figure 13 Optimal Parameters for fabrication of fibers

Two different reduction methods (hydrazine vapours and hydroiodic acid) were used to analyze further the better reduction method. The graphene oxide fibers produced with these optimal parameters resulted in relatively strong fibers that can be controlled by just using the hand. The fibers still need to be handled with care as moderate force can break the fibers apart. Figure 14 below shows a sample of dried graphene oxide fibers wrapped around a glass rod.

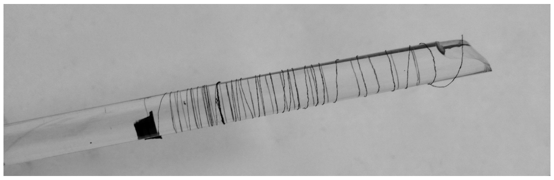


Figure 14 Graphene Oxide fibers wrapped around a glass rod

The hydroiodic acid reduced graphene fiber was more mechanically robust and retained its mechanical flexibility more than the hydrazine vapor reduced graphene fiber. As Pei et al discovered, hydroiodic acid does the best job of reduction without breaking the structure of graphene. Hydrazine vapors in addition to the reduction various functional groups (carboxyl, hydroxyl, etc) produce side reactions like the formation of H2 bubbles, which leads to the degradation of the graphene structure[37].

3.3.2 Scanning Electron Microscopy

Figure 15 below shows the SEM images of the graphene oxide fiber before it was reduced. The average diameter of the graphene oxide fiber is about 160 µm. As evident from the SEM cross-section images at the top right of figure 15, the graphene oxide fiber is made up of stacked sheets aligned together. The cross section shows the packed nature of the graphene sheets. The wrinkles on the side of the fiber are the functional groups present in the graphene oxide fiber[38].

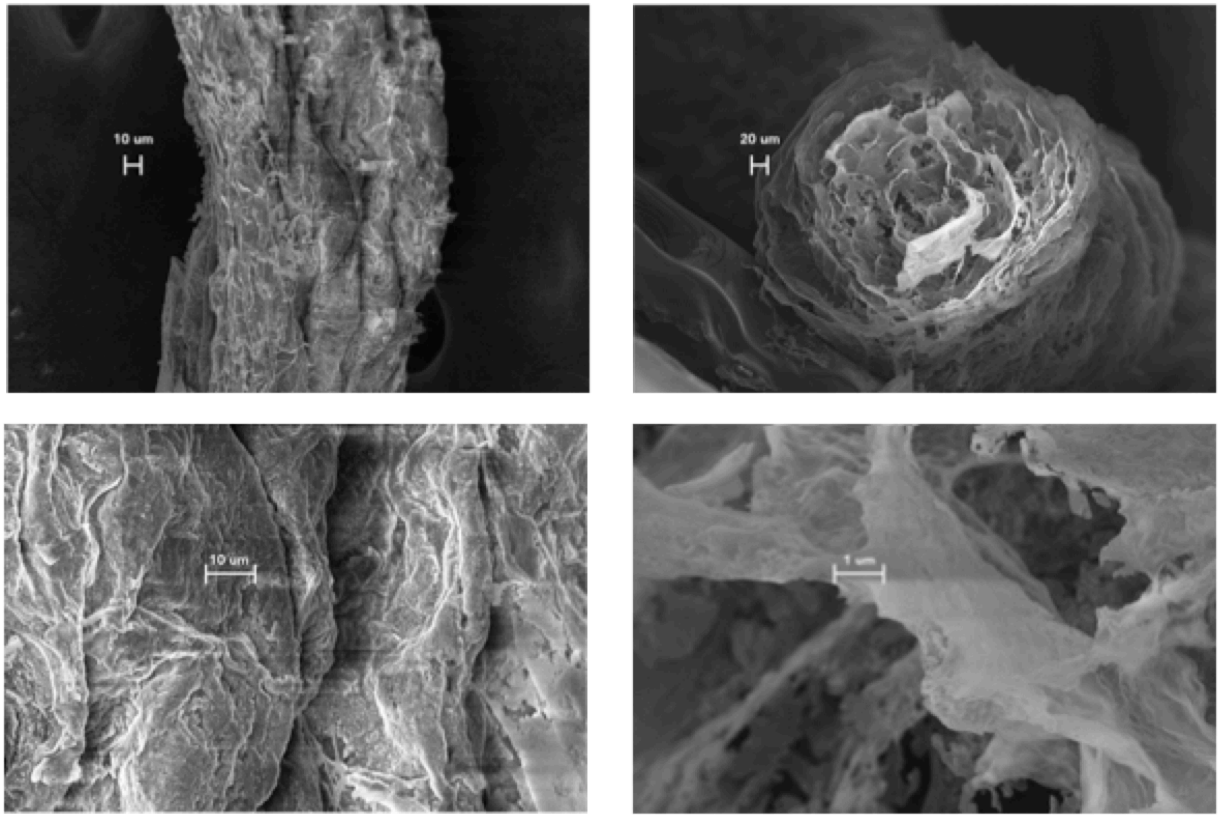


Figure 15 SEM images of graphene oxide fiber

After reduction of the graphene oxide fiber the morphology changes slightly to reveal a fiber with a shrunken diameter and somewhat weaker strength. Flexibility remains however greater caution must be exercised when handling the fibers with hands. Figure 16 below shows the SEM images of the graphene fiber. The fibers now have fewer wrinkles in the outer structure due to functional groups being eliminated through reduction. The average diameters of the fibers are about 50 μm. Figure 17 compares the SEM images of graphene oxide fiber (left) and graphene fiber (right). This side-by-side comparison shows more in depth the shrinkage that occurs when the fiber is reduced to graphene fiber.

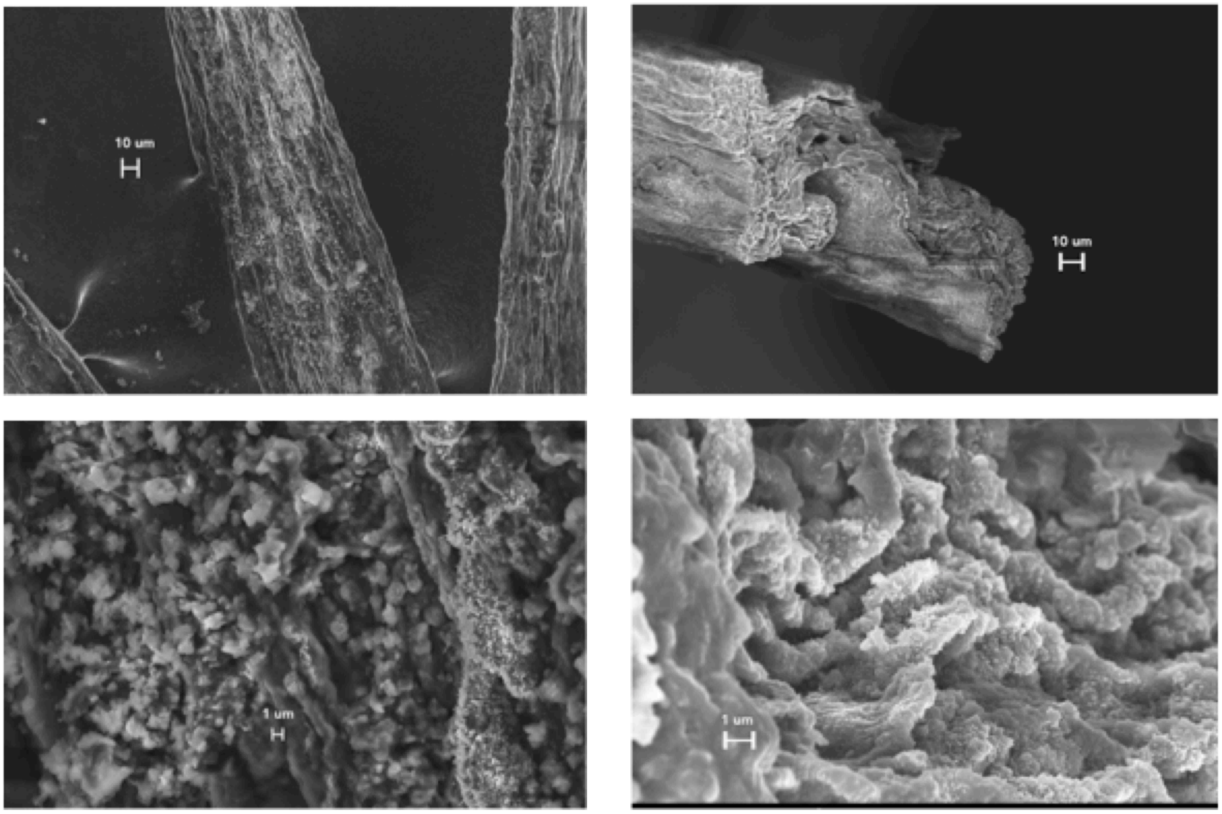


Figure 16 SEM images of graphene fiber (rGO)

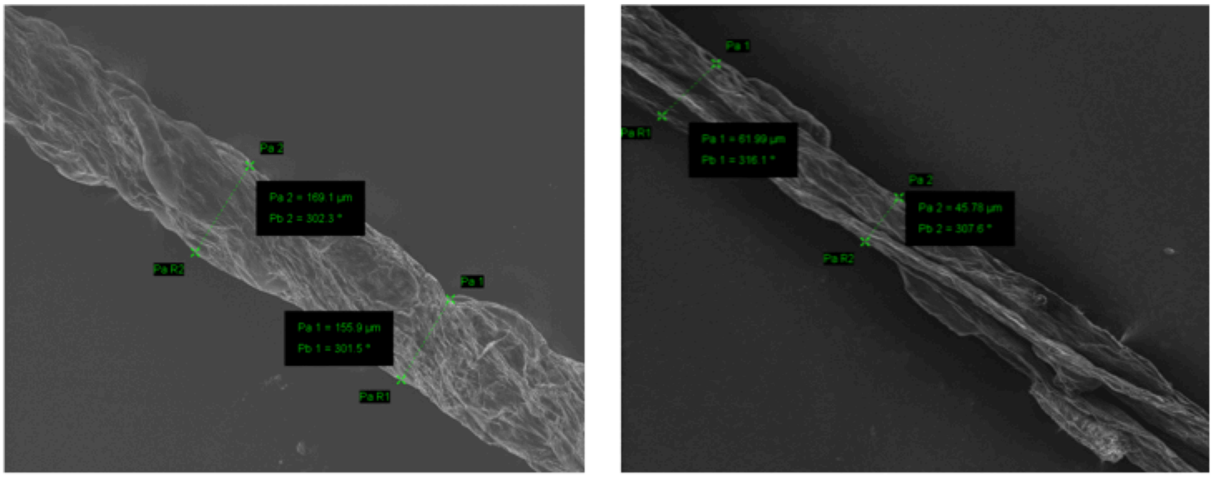


Figure 17 Comparison of GO fiber to rGO fiber

3.3.3 Raman Spectroscopy

The raman plot outlined in figure 18 compares the raman spectra of three different fibers: GO fibers, rGO fibers reduced by hydroiodic acid, and rGO fibers reduced by hydrazine vapours. The most prominent peaks in all the samples are the G and D peaks which lie around 1560 and 1360 cm^{-1} respectively for visible excitation. The G peak is due to the bond stretching of all pairs of sp^2atoms in both rings and chains[39]. The D peak is due to the breathing modes of sp^2 atoms in rings or is known to be a measure of disorder in the sample. When comparing all three samples we can see that the increase of intensity in the ratio between the D and G band (I_D/I_G). This signified a lower defect density for the HI reduced graphene fiber. The increase intensity in the G band also suggests that the sp^2 hybridized carbon network has been partially restored. Thus hydroiodic acid has proven to be the more effective reducing agent in producing the better graphene fiber. Hydrazine vapor has smaller peaks and a smaller I_D/I_G ratio most likely due to the damage inflicted on the graphene fiber structure by the side reactions with hydrazine (H_2 bubbles popping).

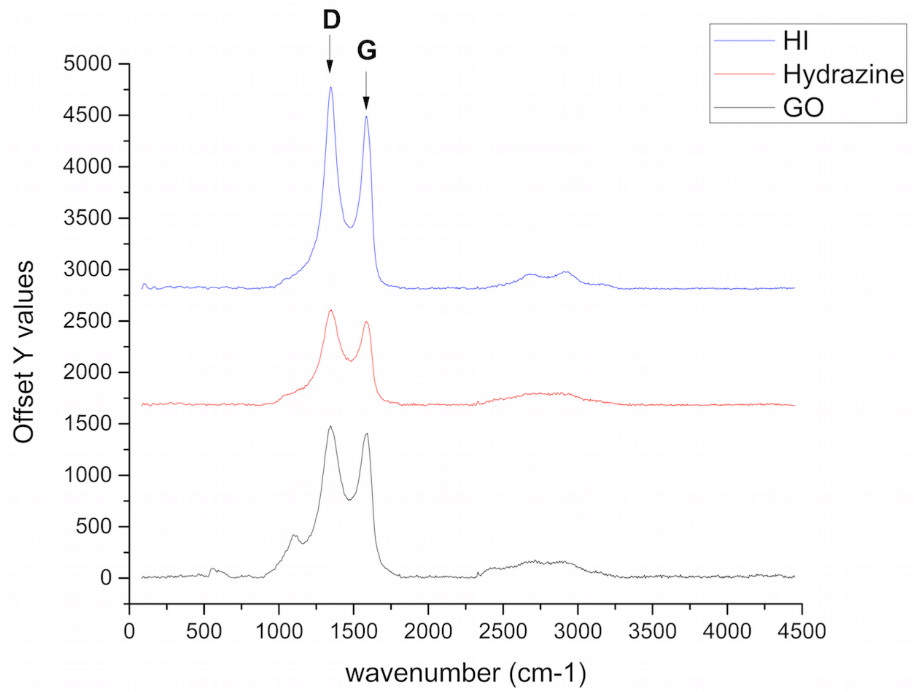


Figure 18 Raman Plot of GO, rGO (HI), rGO(Hydrazine)

3.3.4 EDX

Using the energy-dispersive x-ray spectroscopy unit built into the SEM further analysis was done on the composition of the three fibers: GO, rGO (HI), and rGO (hydrazine). The EDX analysis explains the compositional ratios between carbon and oxygen in the graphene oxide, and the change in ratio after reduction. In figure 19, the left most graph shows 3 major peaks pertaining to carbon, oxygen, and sodium. Oxygen being highest is being contributed to by all the functional groups present in graphene oxide. The sodium peaks are there due to the sodium left on the fibers after coagulation. Since the coagulation bath was made up of 5% NaOH in methanol, after coagulation there were some sodium remaining on the outer surface of the fiber. This is due to the fibers not being washed thoroughly after drying. The second plot in figure 19 shows that after reduction the oxygen peak is greatly reduced due hydrazine effectively removing the functional groups. There are still some sodium left over. The hydrazine vapor method doesn't involve the fiber being put in any solution and thus sodium wasn't washed away completely. The final plot in figure 19 shows the elemental composition after the fibers were reduced with hydroiodic acid. This time the ratio between the carbon and oxygen peaks is even greater, the sodium peak is non-existent and there is some iodine present in the sample. The sodium is probably gone due to the fibers being submerged directly in the HI solution. The Iodine is probably present due HI reacting with hydroxyl groups on the graphene that hasn't been completely removed yet [37].

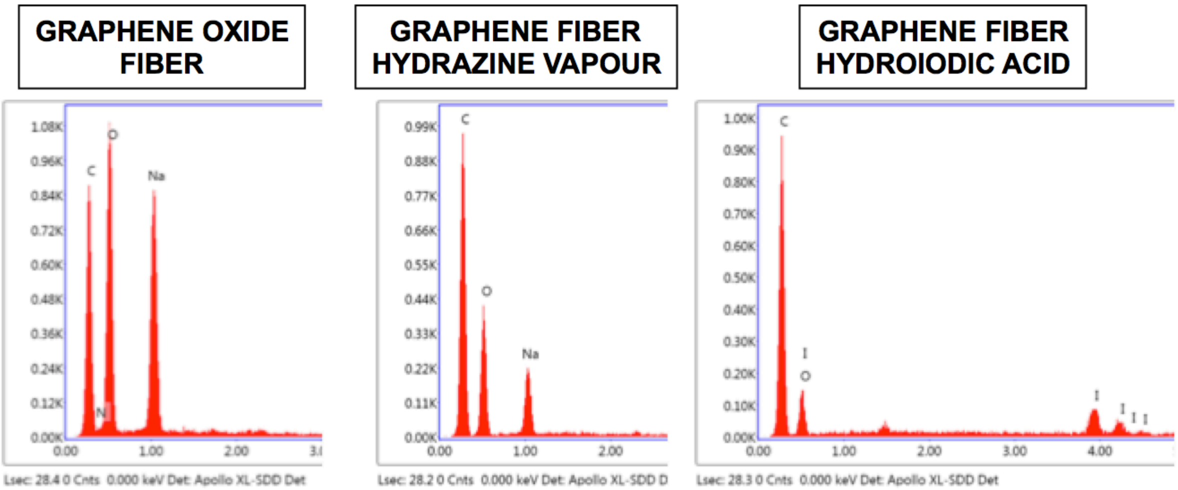


Figure 19 EDX analysis of GO, rGO(HI), rGO(hydrazine)

3.3.5 Cyclic Voltammetry

In order to qualify graphene fiber as a viable option for use as an electrode in supercapacitors it is important to characterize the electrochemical performance by performing cycle voltammetry and obtaining the capacitance at different scanning rates. In order to see the effect of reduction on capacitance, tests were performed on both GO and rGO.

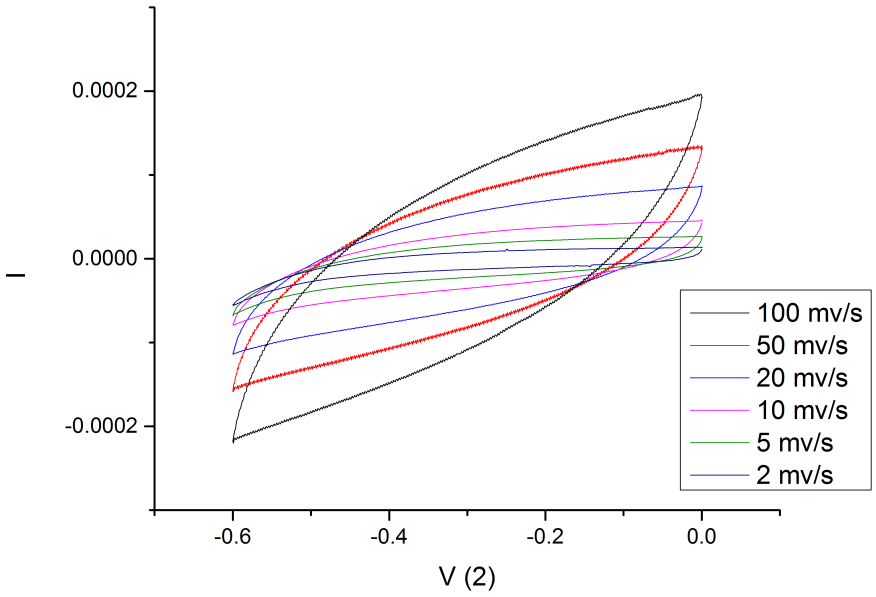


Figure 20 CV curves for GO at various scanning rates

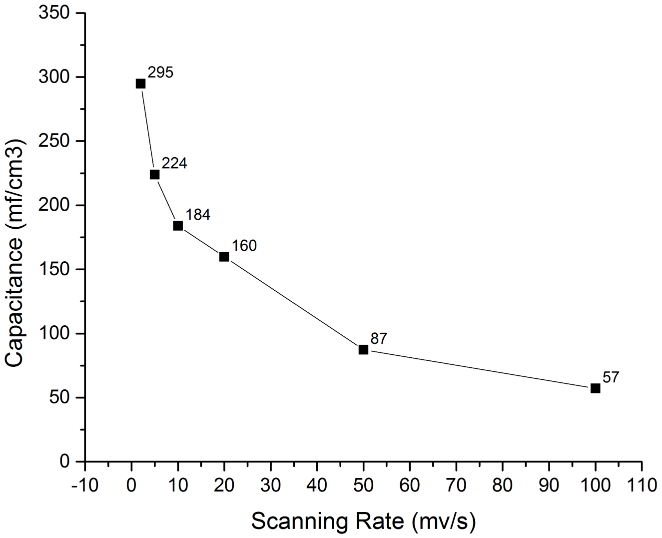


Figure 21 Capacitances at various scanning rates

Figure 20 and 21 show the electrochemical performance of graphene oxide fibers in a half-cell test. The capacitance at a low scanning rate is about 300mf/cm^3 and about 57mf/cm^3 at the highest scanning rate measured (100mv/s). As the scanning rate is increased the capacitance starts to decrease. This is typical of all carbon materials and can be explained by the limited transfer of ions to the carbon particle surface resulting in areas of the electrode layer that are inaccessible at high scan rates [19]. The overall performance is poor, but that is expected due to graphene oxide not being conductive.

After the graphene oxide was reduced, another test was performed to see the effect of reduction on the capacitance. For this method a full cell test was performed on the graphene fiber using PVA gel electrolyte. The full setup is shown in Figure 22.

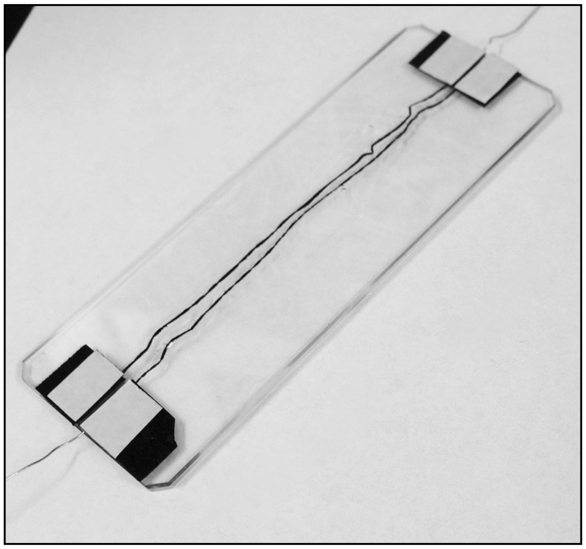


Figure 22 full cell capacitor with graphene fiber

Connecting the graphene fiber electrodes to the potentiostat, cyclic voltammetry was performed to get the following results. The capacitance at 10 mv/s increased to about 2000 mF/cm^{3,} which is about seven times the capacitance of the graphene oxide fiber. This is expected as the elimination of the functional groups restores the sp^2 connection in the graphene network and it turns increases the conductivity of the fiber.

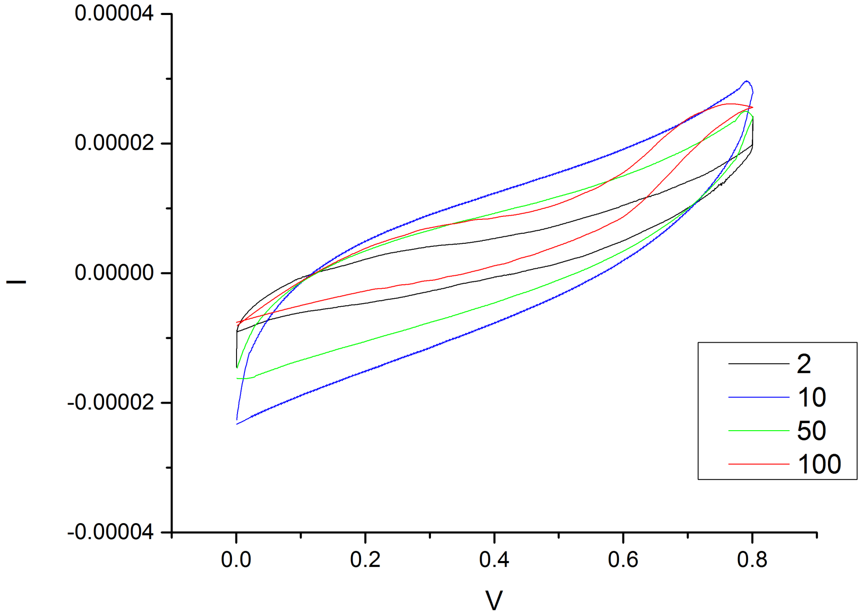


Figure 23 CV curves for rGO at various scanning rates

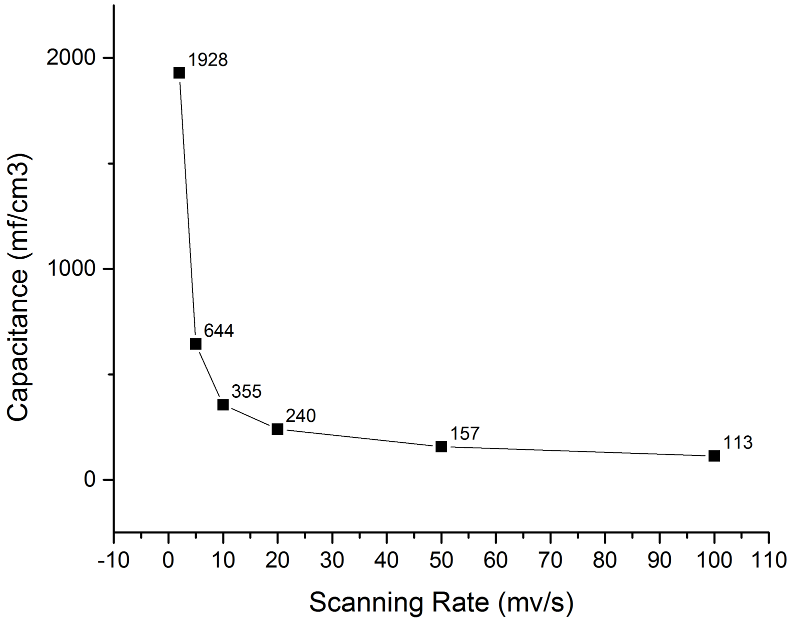


Figure 24 rGO capacitances at various scanning rates

As the length of the fibers used was increased during testing, the capacitance decreased. This can be a result of two major reasons. Firstly as the length of the fiber is increased the linear resistance will also increase, making it less conductive and contributes to a limited capacitance, Secondly the longer the fiber, the more defects that can be present and there may be some disconnects in the material. Since the material is very thing (50 µm) handling it with tweezers and human hand can lead to some form of damage. Wang et al have reported capacitance values for graphene at ~200F/g [40], and although graphene fibers take on a different form factor there is lot of improvement that needs to be done in order for graphene fibers to reach a comparable capacitance level to that of graphene.

3.4 Conclusion & Remarks

Graphene fibers are at the forefront of graphene structures in the 1 dimensionality. Graphene fibers are a cost effective method in produce mechanically flexible fibers that employ properties of graphene. Wet spinning can be used to synthesize graphene oxide fiber, which is later then converted in graphene fibers (rGO) via chemical reduction. My research found that using large flake graphene oxide of concentration greater than 8mg/mL, a syringe needle size of 150 µm, a pump rate of 0.5-1 mL/min, a coagulation bath of 5% NaOH/Methanol will produce robust graphene oxide fibers that can be handled using one's hand. After Raman and EDX analysis it was seen that Hydroiodic acid is the best reduction agent as the fiber retains its mechanical flexibility and strength and the ratio of C:O is significantly higher that hydrazine vapours. The capacitance of graphene oxide fiber yielded capacitances ranging from 57 - 300 mF/cm^3, after reduction the graphene fibers (rGO) yielded capacitances ranging from 110 to 2000 mF/cm^3. The seven-fold increase in capacitance can be explained by graphene fiber (rGO) being more conductive and a better capacitive material due to the sp^2 carbon network structure found in graphene. Although the graphene fiber shows capacitive behavior, the material's structure needs to be further improved to yield electrochemical performances similar to that of other graphene material.

4.0 Chitosan Core Graphene Fiber

4.1 Introduction and Purpose of Study

Graphene fibers although very simple to fabricate using wet spinning methodology need to be improved upon in terms of structural integrity. The graphene fibers tested in this study can be easily damaged by light force of the hand or tools. This low strength in the structure of the graphene also made it particularly difficult to perform electrochemical tests on. As a result a lot of preparation was required to prepare each test. In order to improve the strength of graphene fiber I found that chitosan would be a good substitute in strengthening the fiber while making it an ideal material for supercapacitors.

Natural polymers like chitosan have received a lot of attention across a range of fields due to it being environmentally friendly, inexpensive, and in relative abundance. Chitin (chitosan being its derivative) is known to be the second most abundant natural polymer [41]. Chitosan is an ideal polymer that can be integrated with this study because it is wet spinnable in the same kind of coagulant bath as graphene fiber. Wet spinning of chitosan fibers from the polymer in its bulk form, involves the dissolution of chitosan in acetic acid to form a dope. When this dope is injected into a coagulant bath, fibers are formed in similar fashion to graphene fiber. Chitosan fibers have proven to be strong after being air-dried. Figure 25 shows chitosan fiber being used to hold up a metal nut weight about 4.6 grams. The purpose of the study is to see if chitosan would be a good additive to graphene fiber, and whether it can contribute to the strength of the wet spin fiber.

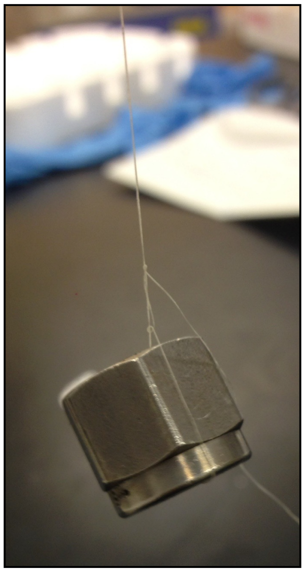


Figure 25 Chitosan Fibers holding up metal nut

Instead of combining GO solution and the chitosan spinning dope, a coaxial spinneret was used. Instead of using a single syringe needle, a coaxial spinneret was used to inject both the GO and the chitosan at the same time but in separate vessels. The inner layer is made up of chitosan and the outer layer is GO.

4.2 Experimental Methods

Using the wet spinning setup already established for the production of graphene fibers, the syringe needles was replaces with a coaxial spinneret. Two syringe pumps were fed to the same coaxial spinneret to push the graphene oxide and chitosan solution through.

Graphene oxide was synthesized using the methods described previously. The chitosan dope was prepared via the following methods; 0.2 grams of chitosan flakes mixed into 10mL 2% acetic acid. 7 mg/ml of GO was loaded into one syringe, and another syringe was loaded with the chitosan dope. The syringes were put onto individual syringe pumps and connected to the coaxial spinneret.

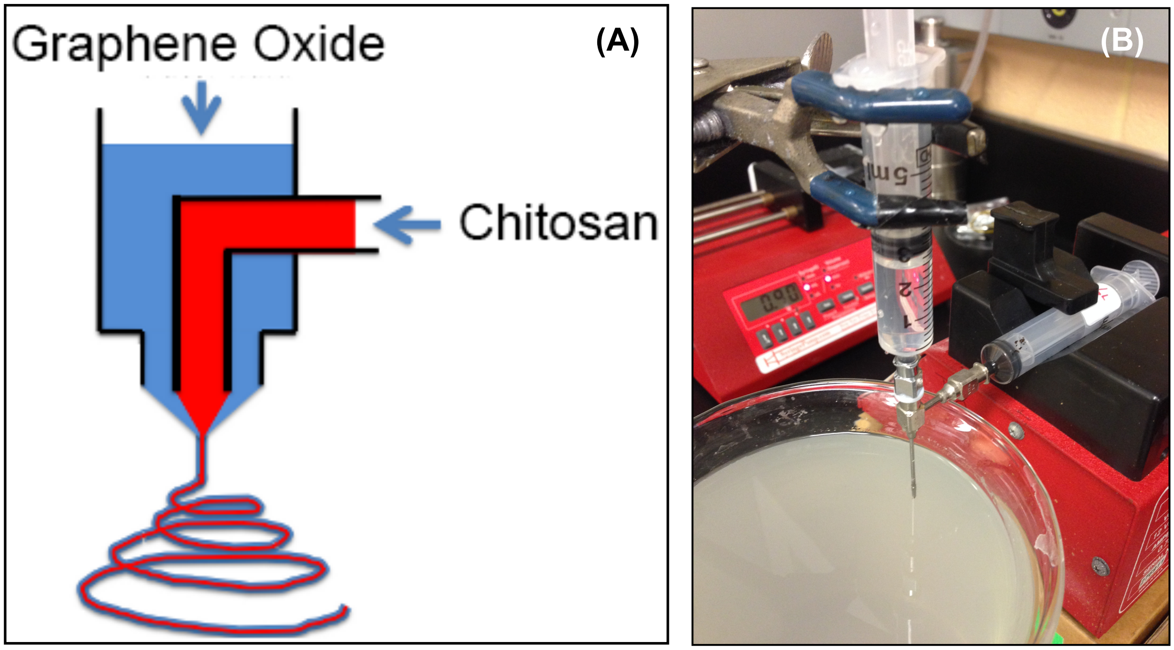


Figure 26 Coaxial wet spinning setup

Figure 26 shows the schematic of the coaxial spinneret. Figure 26a shows the schematic of the inner and outer coaxial compartments. Figure 26b shows a photo of the actual connection with the two syringes connected to two different syringe pumps. The first syringe pump containing the graphene oxide syringe was connected to the outer part of the spinneret, and the second pump containing the chitosan dope was connected to the inner part. The bath used is 5% NaOH/methanol solution as reported before. The pump rate of the outer dope (GO) was set to 1 mL/min, while the inner dope (chitosan) was set to 0.5mL/min. This disparity in pump rates was so that the GO takes priority in coagulating towards the center, as it it’s the more important contributor in electrochemical performance. This would form fibers in the bath with a core of chitosan and an outer shell of graphene oxide. The fibers were then taken out of bath and air dried. The proposed structure of the wet spun fibers look like the schematic outlined in Figure 27. The grey outer layer represents the graphene oxide, and the inner layer is the chitosan core.

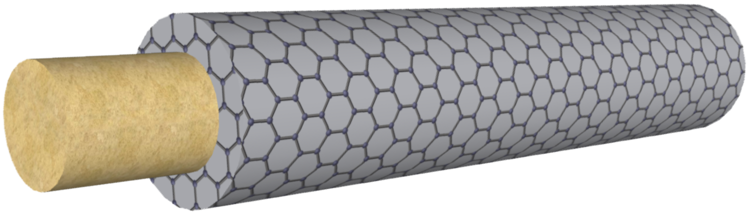


Figure 27 Chitosan-core graphene fiber schematic

To make this as-spun fiber a viable electrode two different steps were attempted. First the fiber was carbonized by putting the fibers in a furnace at 800 °C for 2 hours. This was done to reduce the graphene oxide layer on the outside and to carbonize the center to make it more conductive. The second step was to use hydrazine vapour to chemical reduce the graphene oxide on the outer layer to graphene.

4.3 Results and Discussion

After the dopants were injected into the coagulant bath, it was immediately observed that the chitosan made the process more continuous and smooth. When wet spinning GO fibers on its own, the length of the fibers was limited as after a certain length the overall weight of the fiber cannot be sustained by holding the end of a fiber vertically. However by incorporating chitosan into the core, the fibers were more continuous and fibers of 1 meter in length were successfully fabricated as shown in figure 28. The fibers were also significantly higher in strength than the graphene fiber counterpart.

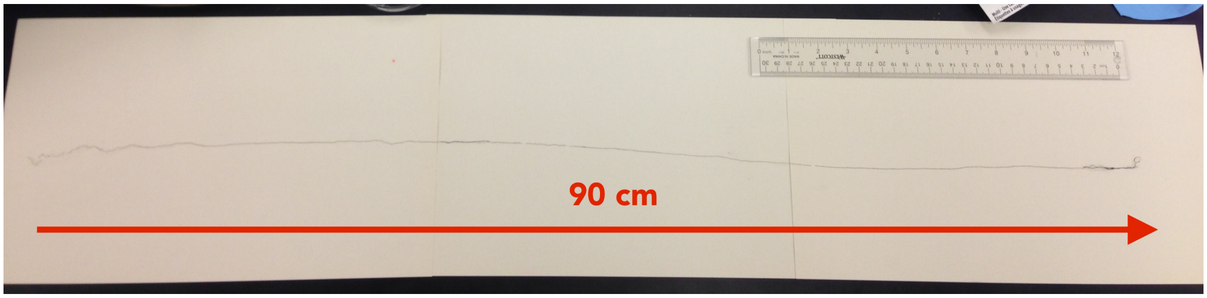


Figure 28 freshly spun chitosan-core GO fiber

However as continuous and structurally sound the fibers were there were two major issues noticed throughout the structure. Firstly the spinneret wasn't always perfectly aligned; the center compartment would sometimes be too close to the outer compartment leading to uneven GO layers around the chitosan core. The misalignment of the spinneret is represented in figure 29b. The second issue with the as spun fibers are the discontinuity in the graphene oxide layer. This is also due to the coaxial needle not being perfectly aligned. The non-continuous pump can lead to variable changes in the pressure of the extrude fiber. The changes in pressure during the wet spinning phases are strong enough to change the alignment of the coaxial spinneret. Another reason the graphene oxide layer can be non continuous is the chitosan fiber is not chemically attracted to the graphene oxide sheets. Both dopants have a negative charge and attraction is only held together by hydrogen bonding and the inwards coagulation of the wet spinning method.

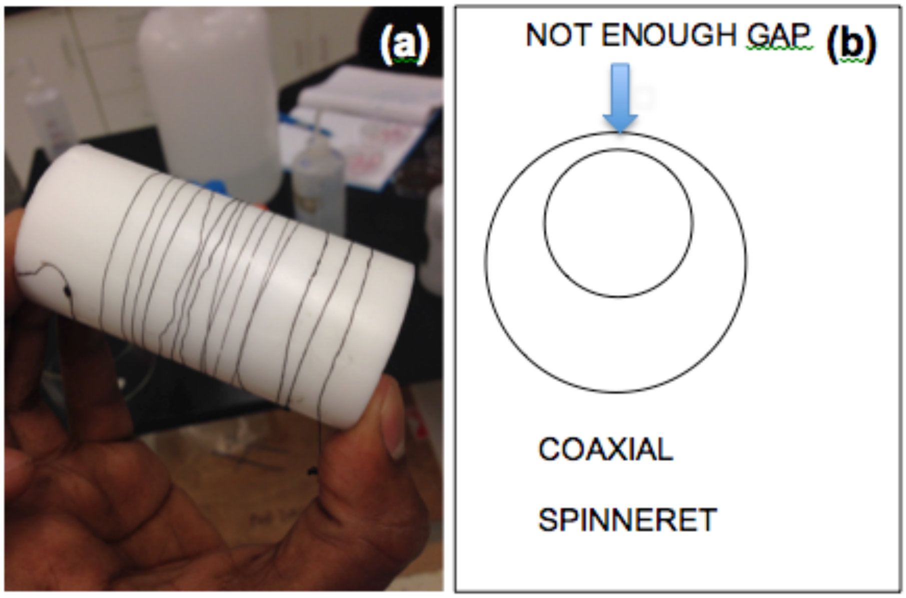


Figure 29 Discrepancies with chitosan-core GO fibers

SEM analysis was used to further investigate the properties of the fibers. As shown in figure 29 (left) the chitosan fibers are very smooth with pieces of sodium that have attached during the coagulation process. The SEM picture on the right in figure 29 shows a cross-sectional view of the chitosan core GO fibers. As one can see the GO is not completely continuous around the core. The GO portion of the fibers has a stacked sheet structure with a plethora of wrinkles as expected and investigated when wet spinning the GO fibers on its own.

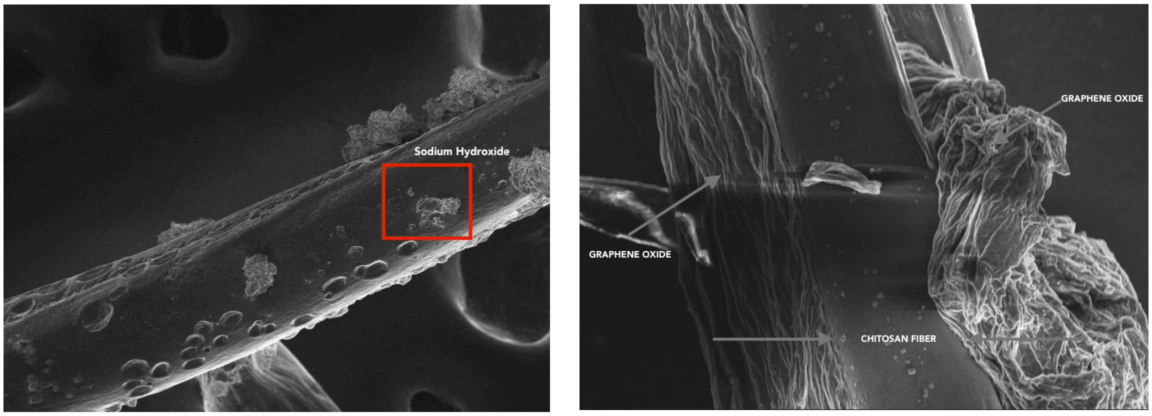


Figure 30 SEM of chitosan-core GO fibers

As mentioned in the experiment methods section the as-spun fibers were either carbonized in a furnace or reduced via hydrazine vapours to make them more suitable as supercapacitor material. In the carbonization method it was found that after treating the fibers in the furnace, all mechanical and structural integrity was completely eliminated. The fibers after carbonization shrunk in size dramatically and had a crisp texture. It was structurally too weak to be tested for capacitance. In the second method the fiber was reduced via hydrazine vapours. This method was successful in keep the flexible nature of the fiber and effectively reducing the GO layer to rGO. However when testing the fibers in an electrolyte solution the chitosan core completely dissolved. The chitosan probable allows for the structure to regain moisture which affects the strength of the material [42].

4.4 Conclusion and Remarks

Chitosan is an excellent natural polymer that can used to strengthen the GO fibers produced using a wet spinning methodology. It coagulates in the same type of coagulation bath and it plays a synergistic role in strengthening graphene fiber. It was used to successfully produce long strands of chitosan-core graphene fibers up to about 1 meter in length. It was structurally improved compared to standalone graphene fiber, however it had few discrepancies. Firstly the coaxial needle is not guaranteed to be perfectly aligned all the time and can produce an uneven GO layer. Secondly patches of GO can be missing due to the misalignment of this spinneret and due to the chemical composition of GO and chitosan. After attempting to carbonize the chitosan-core GO fiber to a carbon based graphene fiber, the fiber lost its mechanical flexibility and became very crisp. This rendered the material a poor electrode for fiber based supercapacitors. Reducing the GO layer with hydrazine vapours was successful and did not affect the mechanical flexibility, however testing the fiber in electrolyte deemed to be ineffective as the chitosan dissolved in the solution due to poor wet strength.

5.0 Summary and Future Direction

Since its discovery graphene has become the cornerstone for many research ideologies. Its superior properties make it the ideal centerpiece for many of the world's applications and in particular: electrochemical storage. With the world quickly shifting away from petroleum based power to environmentally friendly initiatives such as batteries and supercapacitors, graphene is become a key player in making this happen. Graphene currently exists in many different forms at many different dimensionalities but its foray into the 1 dimension as graphene fibers is in the infant stages. In this study graphene fiber was fabricated using the age-old method of wet spinning. By using graphene oxide as the dope, fibers were extracted from a coagulant bath to produce graphene oxide fibers. It was found that hydroiodic acid was the best reduction agent to produce graphene fibers that retained their strength and flexibility. Testing the graphene fibers in a full cell setup yielded capacitance values as high 2000 mf/cm^3. The strength and flexibility of the fibers was attempted to be improved by integrated a coaxial spinneret into the wet spinning rig to produce chitosan core graphene oxide fibers. Although successful in producing strong continuous fibers, the material was deemed a poor electrode for flexible supercapacitors.

The future direction of graphene fiber production will be to improve the strength and durability. Although continuous fibers can be produced, irreparable damage can be easily inflicted upon the fibers upon handling. This can be done by two ways. Firstly introducing crosslinking agents or polymers can improve the GO dope that is injected into the coagulant bath, which results in high strength and capacitance. Secondly another polymer can be introduced into the coaxial spinneret to produce fibers that have an inner and outer layer. Combining with another polymer in this fashion will allow GO to retain its original structure and retain the benefits originally present on the polymer. These improvements can bring graphene fibers one step closer to its enormous contribution to the world of flexible electronics.

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