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Research Plan:
Title: The Controlled Production of Graphene Using Automated Mechanical Exfoliation
Category: Materials Science

Rationale

In 2010, the Nobel Prize in Physics was awarded for the discovery of graphene, a new material with unique properties that will one day be used to revolutionize technology worldwide. Graphene is the monolayer form of graphite—it is a single layer of sp^2 carbon atoms in a hexagonal lattice. Graphene is only 0.34 nanometers thin, making it transparent and flexible (Novoselov, 2005). Graphene also has an incredibly tensile strength, and will have applications in stronger, lighter composite materials (Lee, 2008). The carbon bond structure allows graphene to conduct electricity, and it outperforms many traditional materials including copper and silicon (Geim, 2009). Thus, graphene will be used to make electronics faster, transparent, and flexible. These devices will range from superior batteries and capacitors for use in smartphones to next-generation solar cells. While graphene's novel properties will give it a wide variety of applications, they have yet to be realized on an industrial scale.

Graphene's atomic thickness makes it incredibly sensitive to its environment and how its produced. Graphene is typically a semimetal with no bandgap, but this can change depending on how it's produced. For example, when graphene is strained, a bandgap is induced (Geim, 2009). This means that strained graphene behaves as a semiconductor instead of a conductor. Semiconductors require additional energy to conduct electricity. This energy can come from different sources depending on the application; in solar cells, it comes from light, and in transistors, it comes from electricity. Strained graphene will therefore be used in semiconductor applications, but will not function as an electrode that always conducts electricity. To properly research (and one day industrialize) graphene, it must be able to be produced with consistent, controlled performance. Graphene's sensitivity has been a major obstacle that has hindered research, and in turn graphene's application.

With today's production methods, researchers must sacrifice either graphene quality, size, or control to gain another of these qualities. The method that produces the largest size graphene, chemical vapor deposition (CVD), produces low quality, polycrystalline graphene (Mag-Isa, 2015). The method that produces the highest quality graphene, mechanical exfoliation, cannot produce graphene in a controlled manner (Yuan, 2016). Mechanical exfoliation was first used in graphene's discovery in 2004. The near-pristine graphene flakes it produces have been used to discover the material's novel properties, and the method is still being used to discover new phenomena. Although it is the oldest production method, it can still be improved.

Traditional mechanical exfoliation is conducted using Scotch tape, where a graphite crystal is placed on the tape which is then folded and unfolded repeatedly (Huang, 2015). This peels thinner flakes from the graphite crystal. The graphite/tape is then contacted with an SiO_2 substrate, and when the tape is removed flakes remain on the substrate—some of which are monolayer graphene. Although seemingly low-tech, this method produces the highest quality graphene because of the high quality, monocrystalline nature of the graphite (Huang, 2015). However, the method is conducted manually by the researcher. This allows human error to prevent controlled production, as variables such as time, speed, and pressure cannot be reliably kept consistent by even a veteran researcher.

In the first phase of my research (summer 2018), I worked to solve this problem by automating the mechanical exfoliation process via a motorized roller device—removing human error from the process. I used the roller to test the effects of variables that could not be controlled with the manual process: time, speed, and temperature. However, the automated exfoliation process still needs improvement. In the second phase of my research (summer 2019), I will focus on optimizing the production method by testing new variables and determining the optimal production parameters for controlled production of large-area monolayer graphene flakes. These new variables will include pressure between the rollers, the type of tape and graphite, and re-testing temperature—as the roller design may have inhibited its effect on production in Phase 1. Optimizing the automated process to the point where it becomes superior to the traditional method will aid laboratory research, making it easier for researchers to produce high-quality graphene for use in experiments into graphene's novel properties. This will in turn accelerate graphene's application in a wide variety of industries world-wide.

Research Questions:

- What method of SiO_2 preparation will yield the largest graphene flakes?
- Will natural graphite or synthetic highly oriented pyrolytic graphite be more desirable for mechanical exfoliation?
- Will higher temperatures actually affect graphene production?
- What effect will greater pressure between the rollers have on graphene production?

Hypotheses:

- Substrates that have undergone O_2 plasma treatment will yield the largest graphene flakes, as previously seen with the manual method (Mag-Isa, 2015).

- Synthetic highly oriented pyrolytic graphite will produce the largest graphene flakes, as previously seen with the manual method (Huang, 2015).
- Uniformly increasing atmospheric temperature will yield larger graphene flakes but increased tape residue, as seen with the manual method (Huang, 2015)
- Greater inter-roller pressure will yield larger populations of graphene flakes but increased tape residue. The greater pressure will create more friction, and thus more heat, increasing the adhesion of larger flakes (Novoselov, 2005).

Engineering Goals

The goal of the experiment will be to improve the automated roller method of graphene production. In Phase 1 (Summer 2018), the roller was used to test the effects of time, speed, and temperature on graphene production. However, design flaws severely hindered the method. These problems will be solved in Phase 2 (Summer 2019) to optimize the automated exfoliation process. In Phase 1, the holders for SiO_2 chips were obstructive, severely limiting the amount of graphene transferred. The holders will be redesigned to achieve transfer across the chips' entire surface. In Phase 1, the Scotch tape that was used left large amounts of tape residue on the substrate, often covering flakes. Different tapes, with lower adhesion strengths, will be tested to determine if less residue is produced. In Phase 1, the heating element used created very localized heating, and the atmosphere within the roller could not evenly heat because there was no airtight seal. This will be addressed by re-testing temperature in an oven, where the uniform atmosphere will result in better data. Then, it will be determined if temperature has a significant effect enough to warrant more roller redesigns. In Phase 1, the middle roller was secured by hand, so the pressure between the rollers was not exactly consistent. In Phase 2, a torque wrench will be used to provide a set amount of pressure, and different amounts will be tested. Finally, in Phase 1 the bulk graphite which was used was not new, and it was not known how delicately or roughly it had been treated. In Phase 2, new graphite will be acquired and synthetic graphite (highly oriented pyrolytic graphite) will also be tested, with the aim of achieving larger graphene flakes. By combining the learnings from each variable, the production parameters can be engineered to produce the largest quantity of largest-area graphene flakes possible.

Expected Outcomes

- Using SiO_2 chips that have been subjected to O_2 plasma etching will yield the largest graphene flakes. This is because the O_2 plasma is the most aggressive process to remove adsorbents and debris from the substrate surface (Velický, 2015). Previous research has also claimed that O_2 plasma increased the surface energy of the substrate, which led the adherence of larger flakes (Mag-isa, 2015).
- Using highly oriented pyrolytic graphite will produce larger graphene flakes than natural graphite, because highly oriented pyrolytic graphite (HOPG) is designed to have uniform topography and continuous graphite layers (Huang, 2015). It is thought that graphene from synthetic HOPG will be the same quality as graphene from natural graphite because the graphene will still be monocrystalline and derived from high quality graphite.
- When the atmosphere is uniform, a higher temperature will produce larger flakes but more tape residue. The temperature will increase the surface energy of the substrate, strengthening the van Der Waals attraction forces between the substrate and graphene, as well as between the substrate and residue (Huang, 2015). Previous research with the manual method has shown that an annealing step increased the attraction between SiO2

and graphite, increasing the size of graphene flakes (Huang, 2015). However, it is expected that the adhesive tape will begin to degrade at extreme temperatures, as observed in Phase 1 (Summer 2018) with a very localized, intense heat output.

- Greater pressure between the rollers will produce larger quantities of larger graphene flakes, but also more tape residue. In the manual method, light rubbing is used to transfer flakes through friction and pressure (Novoselov, 2005). It follows that greater pressure will increase the friction, and thus the adhesion of graphene and residue.
- Ultimately, knowledge of each variable's effect on graphene production can be combined to create the ideal graphene production environment. This will allow for the optimization of the mechanical exfoliation process and the improved production of graphene.

Procedure

Role of Mentor

The mentor 3D print new roller parts according to the student's designs. The mentor will provide all necessary equipment, including adhesive tapes, graphite, chemicals (acetone, isopropyl alcohol, deionized water, photolithography primer, SPR 3012 photoresist), and laboratory equipment. The mentor will educate the student how to operate all necessary laboratory equipment and safety procedures. For SiO_2 preparation, the mentor will operate the special equipment for photolithography and physical vapor deposition, as these processes are the only available methods to create a coordinate grid on the wafer surface.

Role of Student Researcher

SiO_2 Preparation

- 4-inch diameter 280 nm SiO_2/Si wafers [Silicon Quest International] will be used.
- Wafers will be ultrasonicated in acetone, isopropyl alcohol, and deionized water for several minutes each. This will remove contaminants from the wafer surface.
- The mentor will then conduct photolithography [MA/BA6, Suss MicroTec] and physical vapor deposition [Denton Vacuum Explorer].
    - A grid of Au/Cr numbers will be created, allowing for the easy location of graphene flakes.
- Unique to Phase 2, an etching processes will be tested to determine which increases the surface energy of SiO_2 most, thus yielding larger graphene flakes.
    - O_2 plasma etching [PE-50, PlasmaEtch] will be used for various times, based on success from previous research (Mag-Isa, 2015), and will be conducted by the student.

Manual mechanical exfoliation

- Since the roller will be tested with new forms of graphite and new adhesive tapes, new control groups must be produced using the traditional manual method (Novoselov, 2005).
- Graphite will be placed on the adhesive tape, which will be folded/unfolded repeatedly to produce dense populations of thin graphite flakes. SiO_2 chips will be lightly rubbed into the tape/graphite to transfer flakes.
- This will be performed with highly oriented pyrolytic graphite (HOPG), which is thought to produce larger flakes (Huang, 2015).

- This will be conducted using Nitto Denko brand tape, which has a lower adhesion strength and is thought to produce comparable size graphene with less tape residue (Dicamillo, 2019).
- HOPG and Nitto tape will be tested with the roller, thus necessitating the production of new manual control groups.

Roller mechanical exfoliation

- The roller consists of a 3D printed body and middle roller, and purchased outer rollers, motor, and motor controller.
- The middle rollers, one for the exfoliation step and one for transfer, will both be redesigned for Phase 2.
    - In Phase 1, there were insets on the middle exfoliation roller, left over from a previous test performed by the mentor. These inhibited exfoliation, as perfect contact was not always achieved. This will be replaced with a smooth roller in Phase 2, which will improve the distribution of flakes over the tape surface.
    - The transfer roller in Phase 1 had holders for SiO_2 chips, but they were obstructive and prevented complete contact. In Phase 2, a new chip holder will be designed, leading to the production of more graphene per chip.
- New variables in the exfoliation step will be tested.
    - Different adhesive tapes will be used, including Nitto Denko brand tapes with a much lower adhesive strength than the traditional Scotch brand. New natural graphite will be used, as well as synthetic highly oriented pyrolytic graphite (HOPG), to determine which form produces the largest flakes.

- Other new variables will apply to both the exfoliation and transfer steps.
    - Pressure between the rollers will be kept consistent and manipulated by a digital torque wrench. Temperature will be tested again in Phase 2, after an unsuccessful attempt in Phase 1, in an oven where a uniform atmospheric temperature should affect graphene production.

Optical Microscopy

- An optical microscope [HI-SCOPE Advanced KH-3000, Hirox] will be used to locate and measure potential monolayer graphene flakes on the SiO_2 substrates, as it remains the most efficient and standard method.
- This will make it possible to determine the effects of each variable on graphene production, and to compare the manual and improved roller methods.

Raman Spectroscopy

- The optical microscope cannot confirm which flakes are monolayer graphene, nor determine the graphene's properties.
- A Raman spectrometer [XploRA ONE, Horiba], the industry standard for characterizing graphene (Ferrari, 2013), will be used again in Phase 2.
- The intensity of the D peak, location and splitting of the G peak, and intensity of the 2D peak will be used to determine graphene quality, strain, and monolayer thickness, respectively.

Data Analysis

- Measurement and quantity data from the optical microscope will be input into Origin software. One-way ANOVA statistics tests, chosen for the ability to compare many groups at once, will be used to compare flake sizes and populations between the manual and roller methods, as well as between roller tests. A Bonferroni post-hoc analysis will be used to determine between which groups there is statistical significance.

- Raman spectra data will be collected using LabSpec6 software. A baseline correction will be performed, and the data will be saved as a text document. The data from the text document will be input into Origin, which will be used to smooth and normalize the data (0 to 1), and perform Lorentzian fits on the D, G, and 2D peaks. This will determine the intensities and locations of the three peaks, allowing for graphene characterization. If trends are observed, one-way ANOVAs with a Bonferroni post-hoc will again be used to determine statistical significance.

Risk and Safety

Chemicals that will be used for SiO_2 preparation include acetone, isopropyl alcohol (IPA), deionized (DI) water, a primer, and SPR 3012 photoresist. Acetone, IPA, and DI water will be used to clean the SiO_2 substrates, while the primer and photoresist will be used for photolithography. All work with chemicals will be performed while wearing a coverall lab suit and gloves to prevent contact with skin, and all chemicals will be disposed of in designated fire-proof chemical containers. The Raman spectrometer [XploRA ONE, Horiba] uses a high power 532 nm laser, which could damage eyes. Approved safety glasses that block green light—including 532 nm—will be worn to eliminate risk.

Hazardous Chemicals, Activities and Devices

1. When in the clean room to perform SiO_2 preparation, including photolithography and physical vapor deposition, the mentor will complete the experimental procedures with the

student as an assistant, under supervision at all times. A coverall lab suit and gloves will be worn to protect skin and clothing from chemicals. All chemicals will be poured into the proper fire-safe container for disposal. This will prevent any risk of harm.

2. Before the student performs Raman Spectroscopy, the mentor will educate the student how to safely use the spectrometer [XploRA ONE, Horiba]. When the student independently performs Spectroscopy for the experiment, certified safety glasses will be worn to block a range of green light including 532 nm, the wavelength of the laser. This will eliminate any risk to the eyes from the laser.

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