The Controlled Production of Graphene Using Automated Mechanical Exfoliation

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Abstract

Graphene, the monolayer form of graphite, is an atomically-thin material with unique physical and electrical properties, and a wide range of applications from stronger composite materials to transparent, flexible electronics. Much of current research focuses on discovering graphene's novel properties; this is most effective in pristine samples, necessitating the consistent production of high-quality graphene. Manual mechanical exfoliation, using Scotch tape to peel layers from graphite to produce monolayers, has traditionally been used to produce the highest-quality graphene of any other method. However, it produces low yields of small-sized flakes, and the presence of human variability prevents controlled, consistent graphene production. In this study, a novel motorized 3-roller device was used to automate exfoliation in order to achieve controlled graphene production. The roller method had two steps: exfoliation, where all three rollers were wrapped in adhesive tape in order to cleave graphite; and transfer, where the middle roller was replaced by another roller with holders for SiO_2 substrates. The roller was used to control and determine the effects of eight variables. Through this controlled study, it was determined that a combination of highly oriented pyrolytic graphite, Nitto brand tape, 120s O_2 plasma treatment, short exfoliation/transfer times, fast roller speeds, moderate inter-roller pressure, and higher temperature produced significantly greater quantities of larger graphene flakes ($p<.05$, $p<.01$, $p<.001$). In the future, design changes should be made to the roller to optimize graphene production, and the device should be used to exfoliate other atomically-thin materials with different properties and applications, such as the semiconducting WS_2 and the insulating hBN.

Introduction

Graphene, the monolayer form of graphite, is a new material with a wide range of applications in many fields, with an expected industry of $390 million by 2024 (Shapira, 2016). Many of graphene's applications arise in the form of next-generation transparent, flexible electronics (Geim, 2009). However, the material's conductivity is highly sensitive and current research is focused on developing consistent production methods. Mechanical exfoliation, a traditional production method, yields the highest quality graphene but at the expense of material size, and it is conducted manually so human variability/error prevents the controlled production of graphene (Yuan, 2016). These problems could be mitigated through automating exfoliation, using motorized devices to consistently produce large-area graphene.

Review of Literature

Graphene Properties and Applications

Graphene is made of a single layer of carbon atoms in a hexagonal lattice and is only 0.34 nanometers thick (Figure 1). The material's atomic thickness makes it transparent and flexible, it is impermeable to gases and liquids, and has one of the highest Young's Moduli—a measure of mechanical strength—of any material (Kidambi 2017; Lee, 2008). Graphene also has incredible electrical
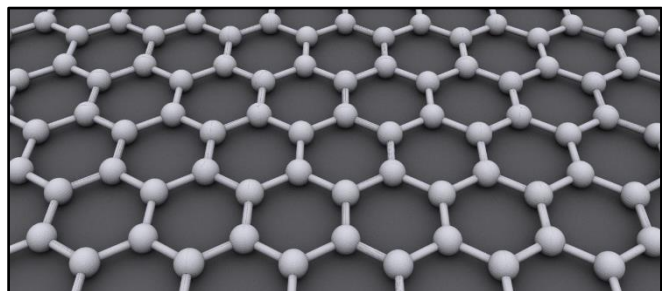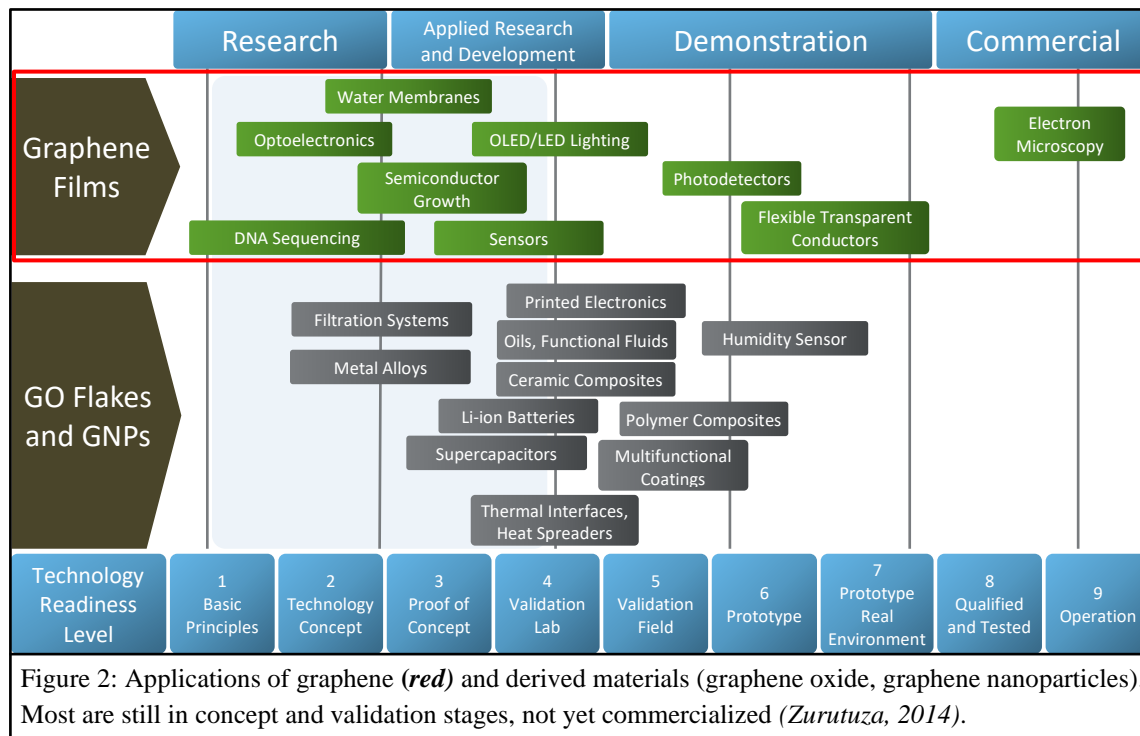

Figure 1: Graphene monolayer structure, a single layer of sp^2 carbon atoms *(physicstuff.com/what-is-graphene/)*.

properties. It outperforms traditional materials such as copper and silicon, and exhibits ballistic transport—where electrons travel without scattering—at room temperature. These novel properties give graphene a wide variety of applications, ranging from DNA sequencing, to nanoelectromechanical resonators, to transparent, flexible electronics (Figure 2; Zurutuza, 2014).

Figure 2 highlights that a majority of graphene applications have been stuck in proof-of-concept and developmental phases. A major barrier to graphene research has been the material's high sensitivity (Yi, 2015). For example, graphene exhibits a strain-induced bandgap; subjecting the material to tensile/compressive strain transitions the material from a conductor to a semiconductor. Therefore, strained graphene can be used in applications like transistors and optoelectronics, but cannot be used in its traditional conductor applications, like electrodes. Graphene's sensitivity necessitates developing production methods that produce graphene consistently and with the desired properties. Developing such methods, while preserving the size and quality of the graphene, has slowed graphene research and application (Yi, 2015).

	Research	Applied Research and Development	Demonstration	Commercial

Figure 2: Applications of graphene (*red*) and derived materials (graphene oxide, graphene nanoparticles). Most are still in concept and validation stages, not yet commercialized (*Zurutuza, 2014*).

Mechanical Exfoliation

Mechanical exfoliation has been used to produce graphene since the material's discovery in 2004. This method exploits the weak Van der Waals attractions between graphite layers to produce monolayer graphene (Novoselov, 2005). A bulk graphite crystal, made of layers of carbon atoms without interlayer bonds, was placed on Scotch tape. The tape was then folded and

unfolded, peeling layers apart to create a dense population of thinner graphite flakes (Figure 3). The tape/graphite was then rubbed onto an SiO_2 substrate to transfer flakes to the substrate, among which monolayer graphene was found. The simple exfoliation process produced the highest quality graphene of any method, due to the bulk graphite's monocrystalline nature (Yi, 2016). However, the method was conducted by hand, so human variability prevented controlled production (Yuan, 2016). Exfoliation also produced relatively-small flakes, so the initial method lacked both consistency and large yields (Huang, 2015).

Figure 3: Large population of graphite flakes on Scotch tape post-exfoliation *(Figure by S. Schutz).*

In the decade after graphene's discovery, researchers attempted to improve exfoliation. Pre-treating the SiO_2 substrates via O_2 plasma etching increased graphene size by increasing the surface energy of the SiO_2, thus strengthening the Van der Waals attraction between graphene and SiO_2 (Huang, 2015; Mag-Isa, 2015). Annealing the tape/graphite/SiO_2 stack on a hotplate before removing the tape to complete transfer increased graphene size as well (Huang, 2015). However, the method was still conducted manually, so the issue of consistency remained.

Automating exfoliation would mitigate this problem, yet very few publications have explored this avenue. One tested a motorized 2-stage device (Figure 4; Yuan, 2016), but only speed was tested as a variable in exfoliation. A benefit of automated exfoliation is the ability to manipulate parameters with a precision beyond human control. The study
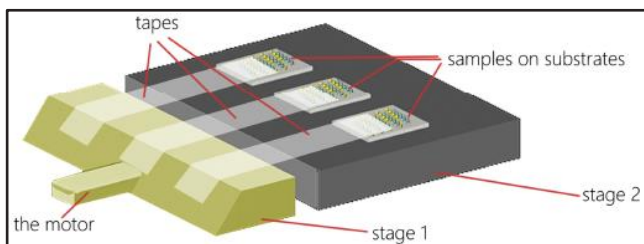

Figure 4: Schematic of the 2-stage motorized mechanical exfoliation device *(Yuan, 2016).*

ignored other variables, such as time and temperature, which remained to be explored. Other publications tested stamping mechanisms, but still with limited efficacy. One started by thinning

graphite via manual tape folding (Mag-Isa, 2015), introducing human variability into the supposedly-automated process. Another exfoliated $MoTe_2$ and $MoSe_2$, 2D semiconducting materials, but not graphene (Dicamillo, 2019). Furthermore, stamping techniques are inherently inefficient, as they require separate motions for contact and removal of the tape/graphite. A novel roller device, however, could achieve continuous, efficient graphene production. A roll-to-roll process (Bae, 2010) was successfully used to transfer graphene sheets from metal to polymer substrates after production via chemical vapor deposition—a production method which sacrifices material quality for size—so a roller shows promise for the exfoliation of high-quality graphene.

Phase 1

Problem Statements

1. Exfoliation is inconsistent because it is conducted manually, but automating the process and manipulating parameters to achieve controlled production has been under-researched.

Objectives

1. To utilize an automated roller device to achieve the controlled production of graphene and to determine the effects of variables on graphene production, including exfoliation time, transfer time, roller speed, and air temperature.

Hypotheses

1a. Increased exfoliation time would produce larger quantities of smaller flakes due to increased flake fragmentation—a natural part of exfoliation (Yi, 2015).

1b. Increased transfer time would produce larger flake populations, due to repeated depositions with each contact between the tape/graphite and SiO_2.

1c. Slower roller speeds would produce smaller flakes, because large flakes would fragment while the tape/graphite and SiO_2 separated (Huang, 2015).

1d. Higher temperatures would increase the flake sizes, because of increased Van der Waals attraction between the graphene and SiO_2 (Huang, 2015).

Phase 2

Problem Statements

1. The initial device's specialized exfoliation and transfer rollers had design flaws which hindered graphene production.

2. There were parameters that Phase 1 did not explore, so the process was not yet optimized.

Objectives

1. To develop new designs for the specialized rollers in order to increase graphene yield.

2. To determine the effects of the remaining parameters: substrate preparation, type of graphite, type of adhesive tape, and re-testing temperature in a uniform atmosphere.

Hypotheses

1. Using transfer roller that secures SiO_2 chips to stages from below, in place of obstructive clamps, would increase the graphene population over the entire SiO_2 area.

2a. Utilizing O_2 plasma to etch the SiO_2 wafers before transfer would increase the surface energy of the substrate, therefore increasing graphene flake size (Huang, 2015).

2b. Synthetic highly oriented pyrolytic graphite would yield larger graphene flakes than natural graphite because of HOPG's uniform topography and larger inter-layer distance.

2c. An adhesive tape with lower adhesion strength would produce graphene with less residue, because the adhesive will not strongly bond to the SiO_2 substrate.

2d. Uniformly increasing air temperature in an oven would yield larger graphene, unlike the localized heating element from Phase 1.

Methodology

Role of Student vs. Mentor

The experiment was conducted over the course of sixteen weeks during the last two summers. The mentor 3D-printed the roller and its parts, provided the necessary materials, and operated the equipment for photolithography and physical vapor deposition. The student independently designed the experiment, including improvements to the roller, conducted all other experimental procedures, and performed data analysis.

Phase 1 (2018)

Pre-Exfoliation Procedure. To best view graphene under a microscope, 4-inch Si wafers with a 285nm SiO_2 layer were used (Blake, 2007). Photolithography and physical vapor deposition (PVD) were performed to deposit coordinate grids that identified graphene locations. For photolithography, a spin coater [Headway Research] created 1μm-thick layers of primer and SPR 3012 photoresist, and a mask aligner [MA/BA6, Süss MicroTec] exposed the wafer and a photomask to UV light for 20sec. PVD [Explorer, Denton Vacuum] was used to deposit 30nm gold on 10nm chromium, and acetone was used to remove the photoresist, leaving coordinate grids on the wafers (Figure 5). The wafers were cut into chips using a diamond-tipped scribe, each with one coordinate grid.
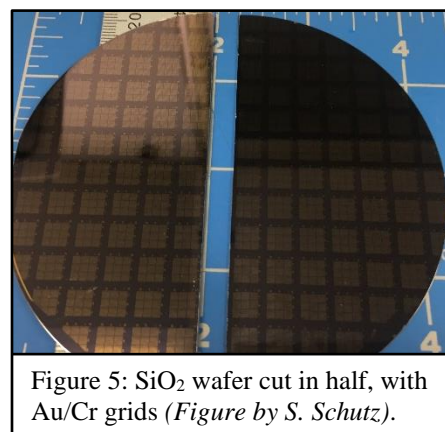

Figure 5: SiO_2 wafer cut in half, with Au/Cr grids *(Figure by S. Schutz)*.

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Automated Exfoliation. A roller device was tested to produce graphene without human error (Figure 6). The device consisted of three rollers, with the middle being interchangeable.

First, all three rollers were wrapped in tape and dabbed with graphite. This left behind flakes, which were exfoliated by the contact/separation of the rollers (Figure 7A). Then, the middle roller was replaced with one with holders for SiO_2 chips. Flakes were transferred to the SiO_2 from the tape by contact as the rollers operated (Figure 7B).
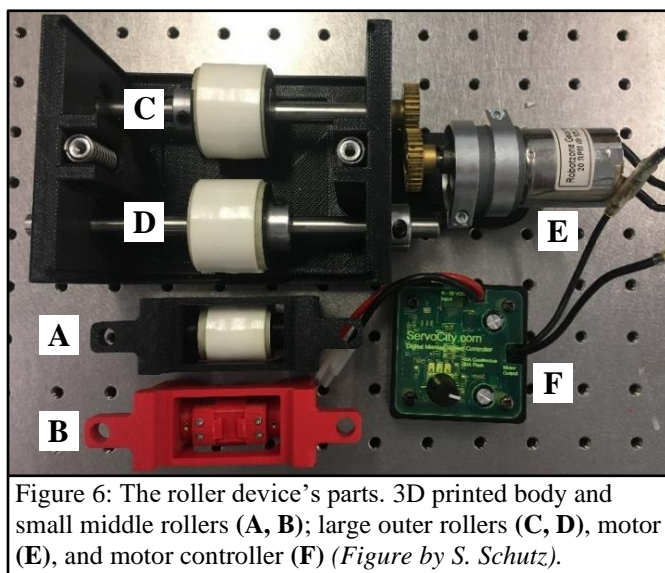

Figure 6: The roller device's parts. 3D printed body and small middle rollers **(A, B)**; large outer rollers **(C, D)**, motor **(E)**, and motor controller **(F)** *(Figure by S. Schutz).*

The roller was used to control variables that are difficult for a human to keep consistent. Varied exfoliation times (30sec-10min) and transfer times (1-6 min) were tested to observe the effect on flake size and population, respectively. Roller speeds of 20rpm (the motor's maximum capacity) and 10rpm were compared. Finally, a heating element located beneath the rollers was used to test exfoliation at a higher temperature (~100°C).

These controlled variables were used to determine the underlying mechanisms behind automated exfoliation. As a control group for comparison with the roller, graphene was produced by the traditional exfoliation process of manual tape folding/unfolding (Novoselov, 2005).
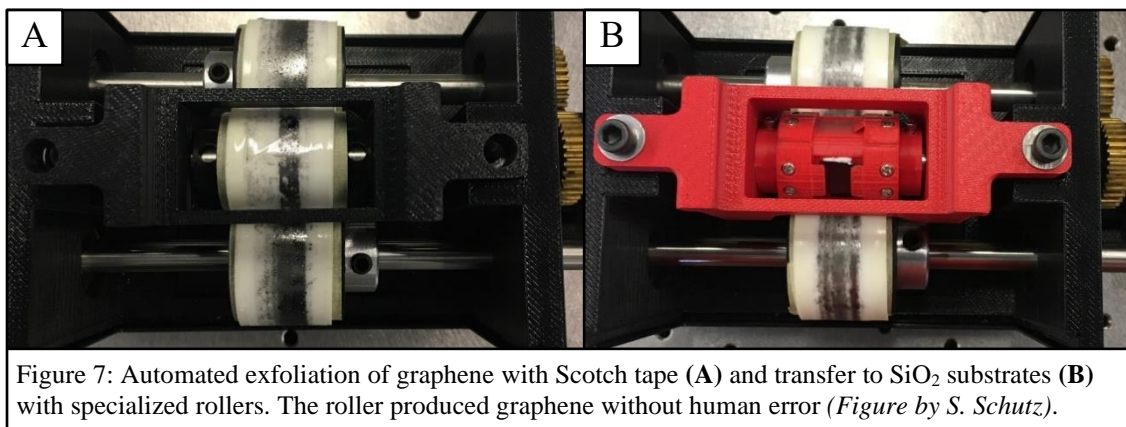

Figure 7: Automated exfoliation of graphene with Scotch tape **(A)** and transfer to SiO_2 substrates **(B)** with specialized rollers. The roller produced graphene without human error *(Figure by S. Schutz).*

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Post-Exfoliation Procedure. After production, it was necessary to locate graphene flakes on the SiO$_2$ substrates. An optical microscope [HI-SCOPE Advanced KH-3000, Hirox] was used to measure and count every graphite/graphene flake within several 150μm x 180μm areas. This was used to determine the effect of each variable on flake size and population. Then, the entire coordinate grid on each chip was searched through in order to locate and measure potential monolayer graphene flakes (Figure 8).
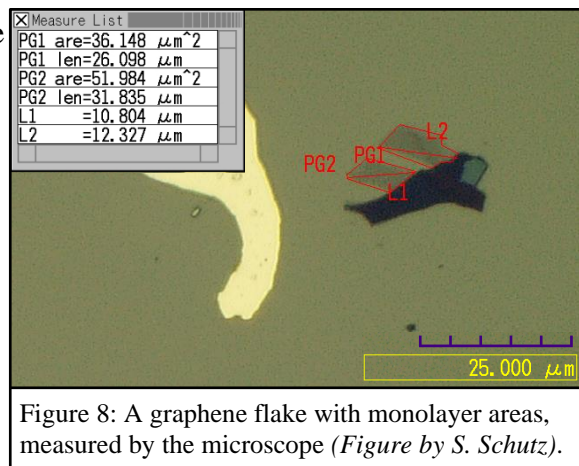

Figure 8: A graphene flake with monolayer areas, measured by the microscope *(Figure by S. Schutz)*.

However, microscopy did not confirm which flakes were monolayer, so a Raman spectrometer [XploRA ONE, Horiba] was used to characterize them. The D, G, and 2D Raman peaks were used to determine material quality, the presence/absence of strain, and flake thickness, respectively (Ferrari, 2006). Figure 9 shows a Raman spectrum with a low D peak intensity, unshifted G peak, and a sharp 2D peak, indicating high-quality, unstrained, monolayer graphene. Alternatively, low quality graphene has an intense D peak, the G peak redshifts and splits with strain, and the 2D peak intensity halves in the bilayer and continues to decrease with increased thickness (Ferrari, 2006). Thus, the Raman spectra were used to observe any effects on graphene's mechanical and electrical properties.
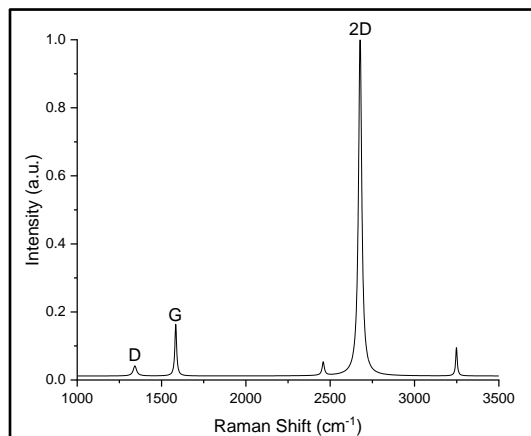

Figure 9: Raman Spectra of a high-quality, unstrained, monolayer graphene flake with labeled peaks *(Figure by S. Schutz)*.

Phase 2 (2019)

  Additions to SiO$_2$ Treatment. The same photolithography and physical vapor deposition methods were used as in Phase 1. However, O$_2$ plasma treatment was added to the process

(Figure 10). O$_2$ plasma had been shown to remove contaminants and increase the SiO$_2$ surface energy, yielding larger graphene (Huang, 2015; Mag-Isa, 2015). The O$_2$ plasma etcher [PE-50, Plasma Etch] was operated at a pressure of 150mTorr, a power of

Figure 10: SiO$_2$ chip exposed to O$_2$ plasma to yield larger graphene *(Figure by S. Schutz).*

98W, and times from 30sec to 120sec. Graphene was transferred to the chips as soon after O$_2$ plasma exposure as possible so the increased surface energy did not dissipate.
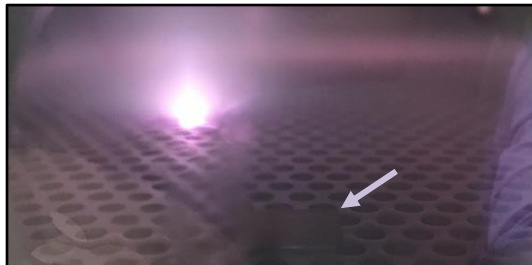
  Changes to Automated Exfoliation. The 3D-printed roller body used was as originally designed by the mentor, but I independently designed key changes to the specialized rollers. In

Phase 1, an exfoliation roller with four insets was reused, causing uneven exfoliation. The new roller was cylindrical and without insets, eliminating the problem (Figure 11). The Phase 1 transfer roller had clamps to secure SiO$_2$ chips, but they obscured the chips and prevented transfer except close

Figure 11: The Phase 2 specialized exfoliation roller *(Figure by S. Schutz).*

to the edges (Figure 12A). This was fixed by my design for a removable chip stage (Figure 12B). Chips were secured from below by foam tape [3M] so they directly contacted the graphite/tape. The stages also safely supported the SiO$_2$ during microscopy and spectroscopy.
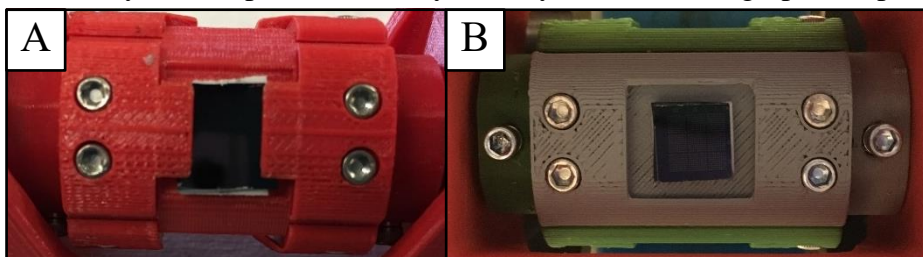

Figure 12: Comparison of Phase 1 (**A**) and Phase 2 (**B**) SiO$_2$ holders for graphene transfer *(Figure by S. Schutz).*

Another problem in Phase 1 was inconsistent inter-roller pressure, as the top roller was secured with screws which were tightened by hand. In Phase 2, a digital wrench was used to make the inter-roller pressure consistent and to test varied torques (10 to 40cNm) in order to determine the optimal value.

While the overall process for operating the roller remained the same, new variables were tested in Phase 2 in order to optimize graphene production. Since Scotch tape [3M] produced large amounts of tape residue in Phase 1, SPV-224 Surface Protection Tape [Nitto Denko] with a decreased adhesion strength was substituted (Figure 13). While natural graphite was originally used, a synthetic form, highly oriented pyrolytic graphite (HOPG), with a more uniform topography was tested in order to produce larger graphene flakes. These changes, coupled with the O_2 plasma treatment, were made in order to produce larger-area graphene.

Figure 13: Nitto tape tested with the for its low adhesion strength. *(Figure by S. Schutz).*
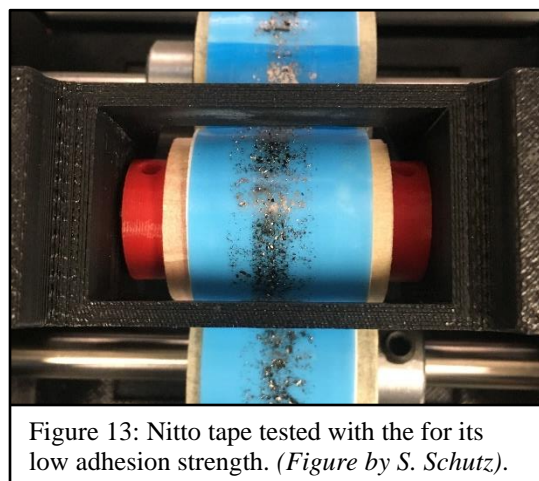
Although previous research with the manual method showed that high temperatures increased graphene size (Huang, 2015), this did not occur with the roller in Phase 1. However, the heating element used did not create a uniformly heated atmosphere, which likely prevented larger graphene production. To fix and improve this, the roller was placed inside an oven [Espec] to produce graphene in a uniform atmosphere, with temperatures ranging from 23°C to 80°C.

The manual method was again used as a control to the Phase 2 roller variables. Thus, O_2 plasma, Nitto tape, and HOPG were used in manual exfoliation. Similarly, optical microscopy and Raman spectroscopy were again used for locating and characterizing monolayer graphene, as they are the most efficient and standard methods for doing so (Blake, 2007; Ferrari, 2013).

Data Analysis

For both Phase 1 and Phase 2, Origin software was used to perform one-way ANOVA statistic tests on flake lengths, areas and quantities. LabSpec6 software was used to collect the Raman spectra data and to perform baseline corrections. Origin was then used to smooth, normalize, and perform Lorentzian fits on the Raman peaks. The peak locations obtained from the fits were compared using one-way ANOVA. One-way ANOVA was chosen for the ability to compare three or more data sets with sample independence, and for all tests a Bonferroni post-hoc was used to determine between which sets there was statistical significance.

Results: Phase 1

The quantities and sizes of graphite/graphene flakes produced by the manual method were compared to flakes from roller exfoliation times of 30sec, 1min, 2min, 5min, and 10min. In 123μm x 98μm areas, the manual method yielded a mean of 17.17 flakes, while the various roller times yielded 17.50, 25.75, 39.75, 45.75, and 46.75 flakes, respectively (Figure 14A). The manual method produced flakes with a mean length of 5.93μm, while the roller produced means of 6.29μm, 6.54μm, 4.39μm, 3.83μm and 3.40μm (Figure 14B). Thus, longer exfoliation times
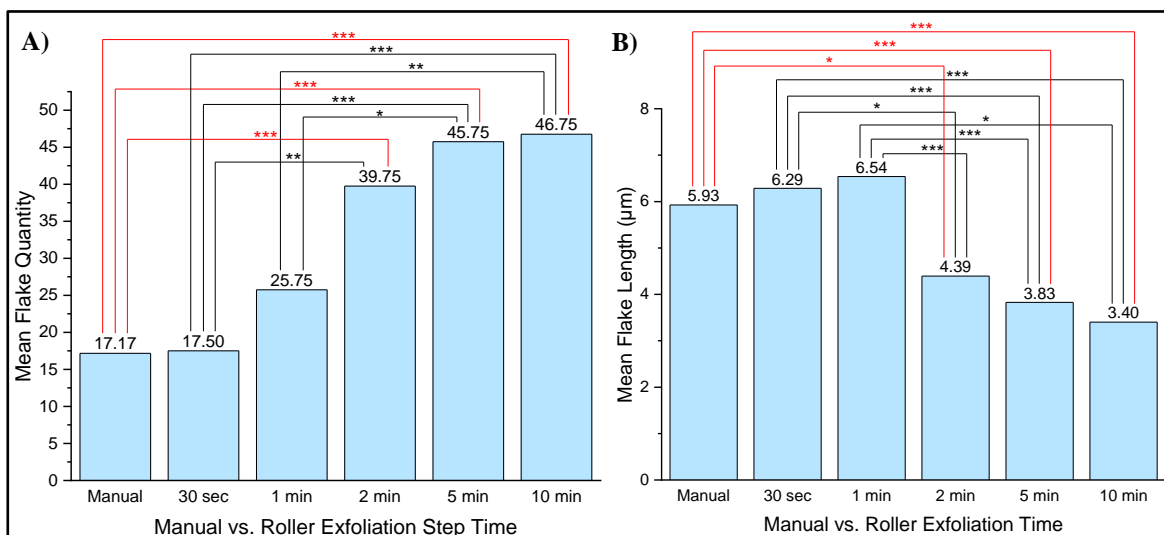

Figure 14: Mean graphite/graphene flake quantities (**A**) and lengths (**B**) for manual exfoliation and increased roller exfoliation times. Quantity significantly increased and length significantly decreased compared to the manual method (**red**) and between roller times (**black**). *$p<.05$, **$p<.01$, ***$p<.001$ *(Figure by S. Schutz)*.
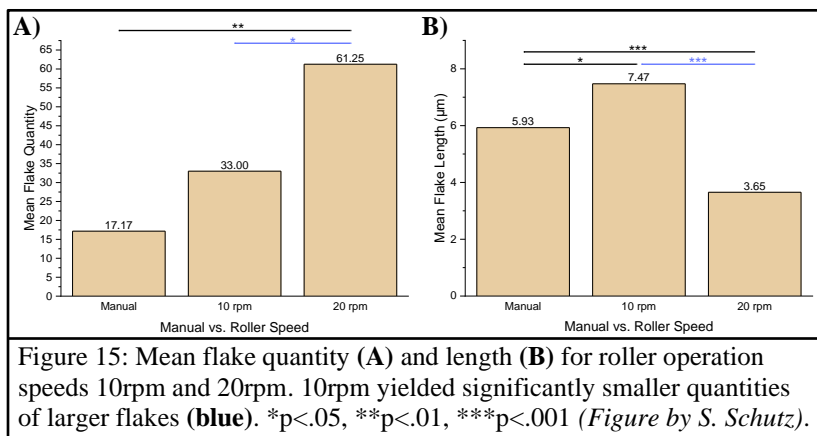
produced significantly larger quantities of significantly smaller flakes, compared to both the manual method (red brackets) and between roller times (black brackets) (p<.05, <.01, p<.001). This confirmed the hypothesis that longer exfoliation time would increase flake fragmentation.
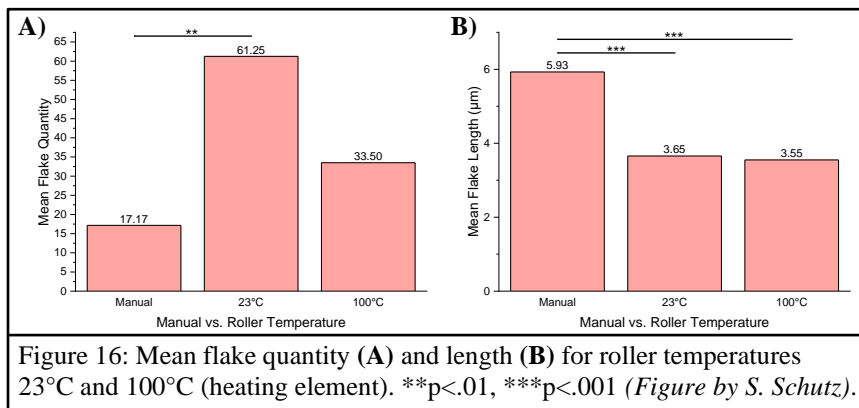
Then, the effect of transfer time was varied through six consecutive 1-min transfers. Microscopy measurements from the same SiO_2 chip areas showed no significant accumulation of flakes, nor significant change in flake size with each additional minute of transfer. It was observed that individual flakes were both deposited and removed during each minute, refuting the hypothesis that longer transfer times would yield larger flake populations.

The roller was then operated at 10rpm with exfoliation/transfer times of 10min and at 20rpm with times of 5min in order to preserve the number of revolutions. 10rpm and 20rpm produced mean graphite/graphene flake quantities of 33.00 and 61.25, respectively (Figure 15A; p<.05). 10 rpm produced flakes with a mean length of 7.47μm, significantly larger than the 20rpm mean of 3.65μm (Figure 15B; p<.001). This refuted the hypothesis that 10rpm would yield smaller flakes. However, the 10rpm samples had large amounts of thick tape residue. Thus, 20rpm was preferred, as flakes surrounded in residue would not be usable in experiments or applications, because the residue would impede graphene's electrical conductance.

Figure 15: Mean flake quantity (**A**) and length (**B**) for roller operation speeds 10rpm and 20rpm. 10rpm yielded significantly smaller quantities of larger flakes (**blue**). *p<.05, **p<.01, ***p<.001 *(Figure by S. Schutz)*.

Finally, the effect of temperature was tested via a heating element placed below the rollers and set to ~100°C. The heater was given 5 min to heat the air before both the exfoliation and transfer step. The 23°C and 100°C tests produced a mean quantity of 61.25 and 33.50 flakes, respectively (Figure 16A). Tests at 23°C produced a mean flake length of 3.65μm, while 100°C produced a mean of 3.55μm (Figure 16B). Neither trend was statically significant, refuting the hypothesis that a higher temperature would yield larger flakes. Furthermore, the higher temperature also visibly increased the amount of tape residue.

Figure 16: Mean flake quantity (**A**) and length (**B**) for roller temperatures 23°C and 100°C (heating element). **p<.01, ***p<.001 *(Figure by S. Schutz)*.
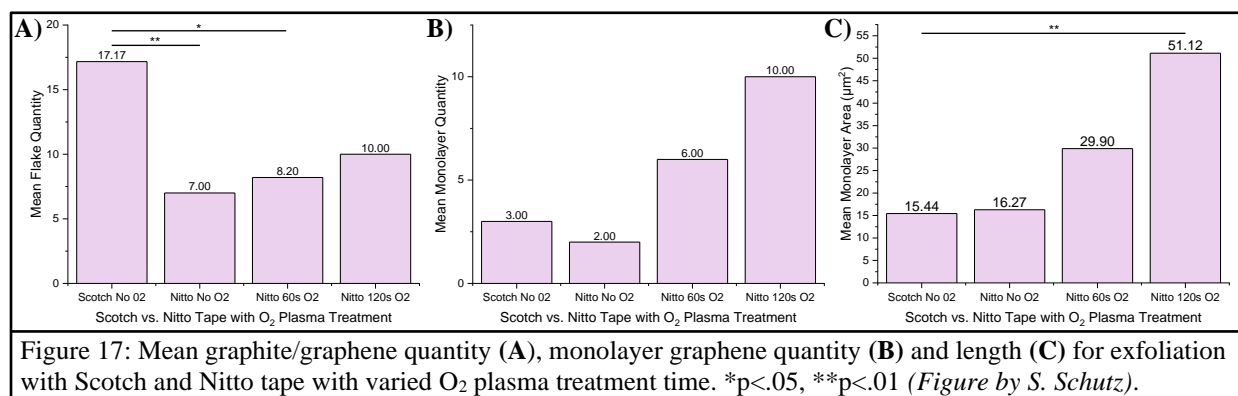
Discussion: Phase 1

The initial experiment successfully determined the effects of four variables on graphene exfoliation, and the Raman spectra of manual-produced and roller-produced monolayer graphene showed no significant difference (p>.05). Thus, the roller's ability to achieve the controlled production of high-quality graphene with limited human intervention was demonstrated. However, as previously mentioned, aspects of the roller design hindered production. The SiO_2 chip holders were obstructive and limited graphene yield. The flawed high-temperature setup, with localized heating and no airtight seal, prevented the significant effect seen in literature (Huang, 2015). Also, human intervention was not entirely eliminated, as the screws securing the top roller were manually tightened. Finally, the graphene produced by both the manual and roller methods was smaller than other reported sizes (Huang, 2015; Mag-Isa, 2015). These problems were addressed in Phase 2, as well as the exploration of four new variables.

Results: Phase 2

The Effects of Four New Variables

      The first variables explored were the use of O_2 plasma treatment and exfoliation using

Nitto tape. Nitto tape yielded a mean quantity of 7.00 graphite/graphene flakes per area,

significantly fewer than the 17.17 from Scotch tape (Figure 17A; p<.001). The weaker adhesive

removed less flakes from the bulk graphite, but left very little tape residue on the SiO_2,

confirming the hypothesis that Nitto tape would produce less residue. Nitto tape was preferred

over Scotch tape, although it yielded fewer flakes, because producing many flakes covered in

tape residue does not improve graphene production. Longer O_2 plasma treatments increased the

mean monolayer graphene quantity from 2.00 to 10.00 (Figure 17B; p>.05) and significantly

increased the mean monolayer area from $16.27\mu m^2$ to $51.15\mu m^2$ (Figure 17C; p<.01).

As hypothesized, O_2 plasma increased the SiO_2 surface energy and strengthened the graphene-

SiO_2 Van der Waals bond, making it a viable method for producing larger graphene flakes.

Figure 17: Mean graphite/graphene quantity (**A**), monolayer graphene quantity (**B**) and length (**C**) for exfoliation with Scotch and Nitto tape with varied O_2 plasma treatment time. *p<.05, **p<.01 *(Figure by S. Schutz)*.

      Next, a digital wrench was used to vary the torque applied to the screws that secured the

top roller in order to manipulate inter-roller pressure. Torques of 10cNm, 20cNm, 25cNm,

30cNm, 35cNm, and 40cNm were tested. Figure 18 shows 10-25cNm, as torques ≥30cNm

prevented rolling. The mean flake quantity significantly increased with pressure (Figure 18A;

p<.05, p<.01, p<.001) with no significant effect on flake size (Figure 18B; p>.05). The roller
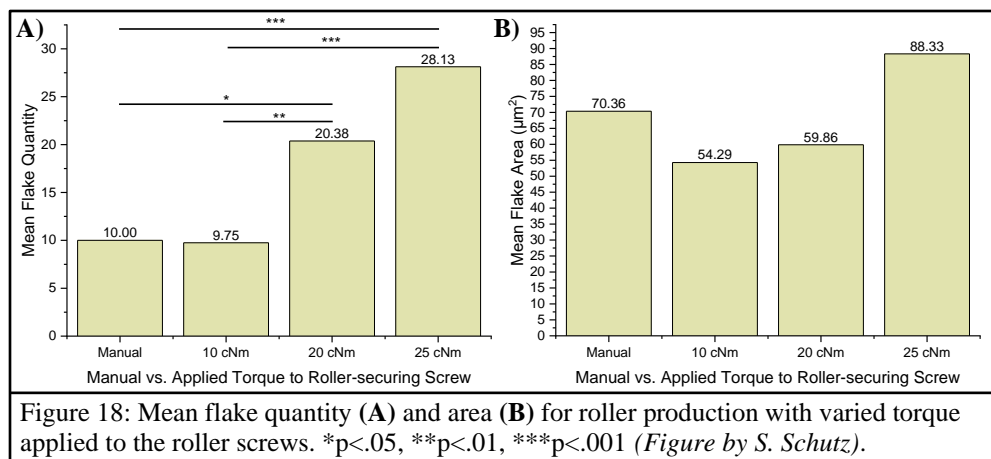
rotated slower than

20rpm at 25cNm,

so 20cNm was

preferred to

preserve the

maximum speed.

Figure 18: Mean flake quantity **(A)** and area **(B)** for roller production with varied torque applied to the roller screws. *p<.05, **p<.01, ***p<.001 *(Figure by S. Schutz)*.

Once the mechanics of the roller method were fine-tuned, a new form of graphite was

explored. Highly oriented pyrolytic graphite (HOPG) is a synthetic graphite with uniform

topography and well-aligned crystals. When the square HOPG bulk was pressed onto Nitto tape

and removed, it usually left behind a flake the same area as the bulk, far superior to the small

pieces left behind by natural graphite. This led to HOPG yielding significantly larger flakes than

natural graphite (Figure 19A; p<.01). Furthermore, images showed that thin flakes appeared in

isolation with natural graphite (Figure 19B), but appeared in large groups with HOPG (Figure

19C). Thus, it was easier to locate thin—and by extension monolayer—graphene on exfoliated

HOPG samples, and there was more graphene on each SiO_2 chip, as proven by Raman

spectroscopy. Together, these results revealed that HOPG was far superior to natural graphite.

Figure 19: The mean graphite/graphene quantity for samples exfoliated from HOPG was significantly larger than that for natural graphite (**p<.01) **(A)**. Images of monolayers **(red)** from natural graphite **(B)** and HOPG **(C)**. Thin flakes appeared in isolation with natural graphite but appeared in large groups with HOPG *(Figure by S. Schutz)*.
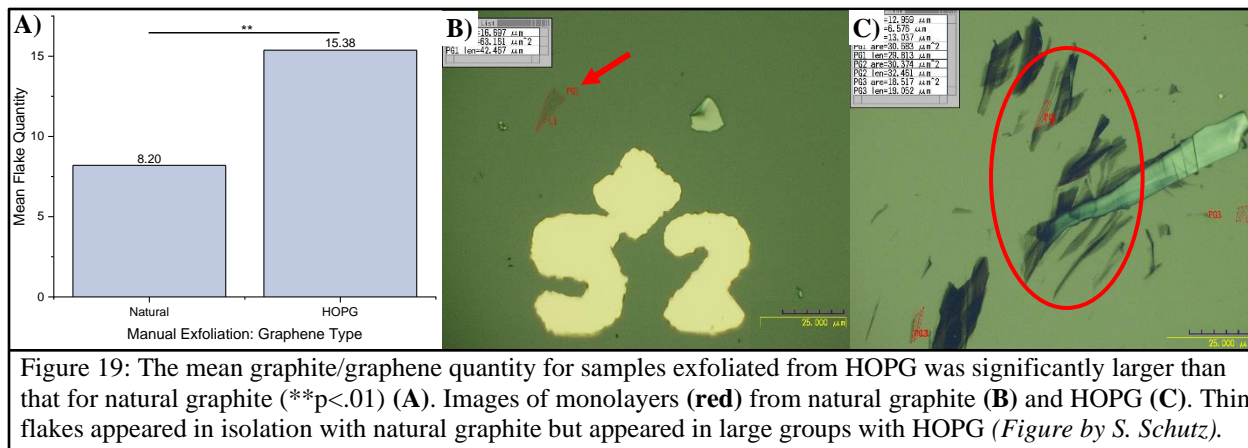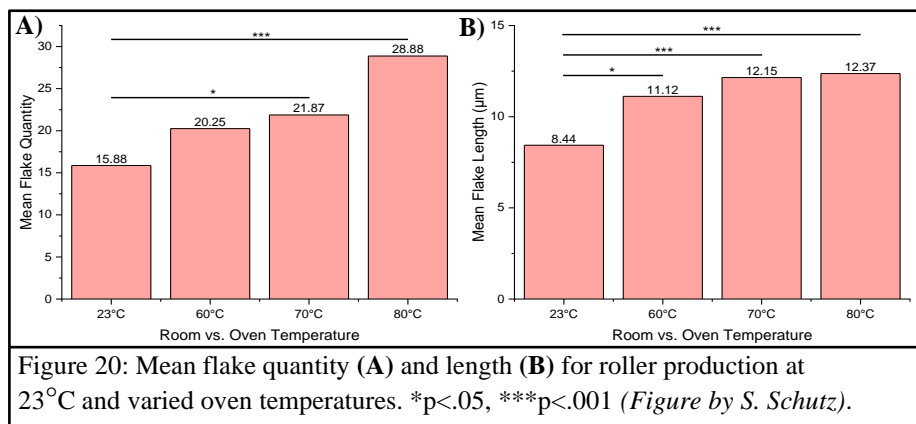
However, these large groups of thin flakes were not observed on chips where the roller was used to exfoliate HOPG. It was determined that this problem originated from the roller transfer process, as conducting manual transfer with roller-exfoliated HOPG/tape did produce the thin-flake groups. Thus, the second half of Phase 2 was dedicated to improving roller transfer.

Efforts to Improve Roller Transfer

First, it must be noted that the new SiO_2 chip stage was effective. Securing the SiO_2 from underneath with foam tape allowed for unobstructed flake transfer, and no chips detached or cracked. The final inset depth was 0.030in, allowing the chips to protrude slightly and contact the graphite/tape on the outer rollers. However, the transfer of thin-flake groups had to be achieved.
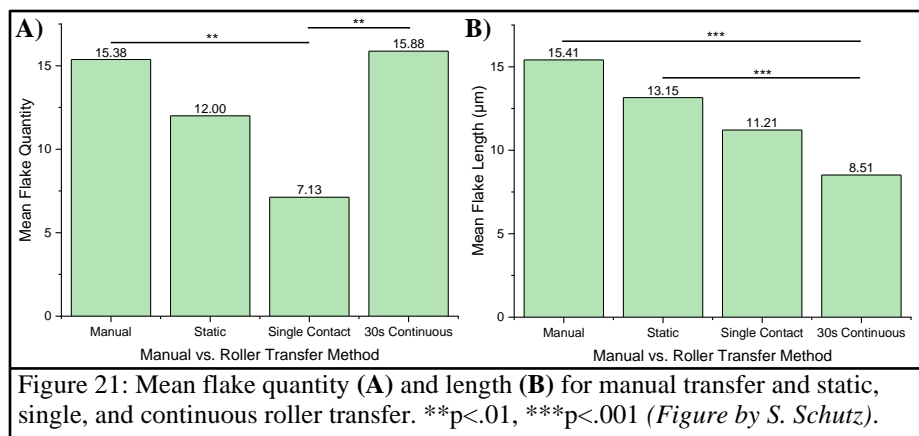
Previous literature reported that an annealing step on 100°C hotplate during manual transfer increased the SiO_2 surface energy and thus the SiO_2/graphene Van der Waals bond (Huang, 2015). This was not observed in Phase 1, but temperature was re-tested in Phase 2 for the possibility that increasing the surface energy would produce the desired thin-flake groups. The new approach, using an oven to provide a uniform atmosphere, successfully confirmed the Phase 1 and Phase 2 hypotheses that higher temperatures would yield significantly larger quantities of significantly larger flakes (Figure 20; p<.05, p<.001), as seen in literature (Huang, 2015). However, the thin-flake groups were still not observed, so I independently developed two variations on the roller transfer method.

Figure 20: Mean flake quantity **(A)** and length **(B)** for roller production at 23°C and varied oven temperatures. *p<.05, ***p<.001 *(Figure by S. Schutz)*.

For "static transfer," the top roller holding the SiO_2 chips was secured at 20cNm with a chip contacting the graphite/tape on one outer roller. This position was held for a minute, during which flakes were transferred to the chip, then the top roller was removed. For "single transfer," the roller was operated for only 0.5 revolutions, meaning each chip contacted graphite/tape only once. Single contact, compared to the manual method and 30s rolling, produced significantly fewer flakes (Figure 21A; $p<.01$) and no thin-flake groups, and was therefore eliminated as an alternative. Static transfer yielded mean flake quantities and sizes insignificantly different than the manual method (Figure 21B; $p>.05$), and once successfully produced the thin-flake groups.

However, this success was not replicated, and static transfer was found to be unreliable. Thus, roller transfer was not successfully optimized.

Figure 21: Mean flake quantity (**A**) and length (**B**) for manual transfer and static, single, and continuous roller transfer. **p<.01, ***p<.001 *(Figure by S. Schutz)*.

Discussion: Phase 2

In Phase 2, the effects of four new variables were determined, and temperature finally yielded the predicted effect. Raman spectroscopy of manual and roller-produced monolayer graphene, from both natural graphite and HOPG, showed the same G peak location and negligible D peak, indicating high-quality, conductive graphene (Figure 22; Mohiuddin 2009).

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Thus, Phase 2 further demonstrated the potential of automated mechanical exfoliation for reliably producing high-quality graphene. However, the novel roller device was unable to transfer the thin-flake groups seen in the manual method when using HOPG. This was most likely due to the geometry of the device, as the round roller did not uniformly contact the flat substrate, and the prolonged contact of the manual method was
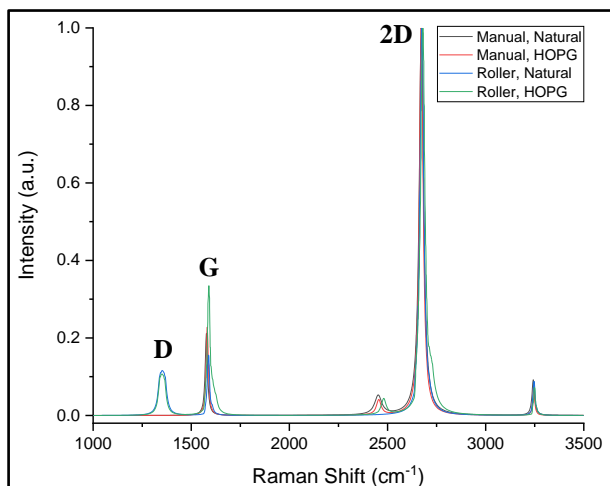

Figure 22: Normalized Raman spectra of monolayer graphene produced by the manual and roller methods from natural graphite and HOPG, showing no major difference between the methods *(Figure by S. Schutz)*.

not simulated by the continuous rolling. This explains why static transfer yielded the thin-flake groups once: the chip must have been tangential to the outer roller for the entire minute of contact. This also explains static transfer's unreliability, as the SiO_2 may have been at an angle in the other trials. Ultimately, it can be concluded that while rollers are the most efficient method for exfoliating graphite, they are inefficient for transferring graphene.

Implications

Through the use of a novel roller device, this study explored automated mechanical exfoliation in detail heretofore unreported in literature, and demonstrated automated exfoliation's potential for improving the production of graphene. Removing human intervention from the process allowed for the control of time, speed, temperature, and inter-surface pressure, and the use of O_2 plasma, Nitto tape, and HOPG yielded larger graphene monolayers. Thus, automated exfoliation was shown to be an effective method for both controlling and improving graphene production. This knowledge will aid research groups worldwide, as they rely on manual exfoliation to produce the high-quality graphene needed for experimentation (Velický, 2015).

While the roller device itself was inhibited by the transfer process, it confirmed that automated exfoliation should continue to be explored in depth, as its use will advance graphene research. When large, high-quality graphene can be easily produced in the lab, research will advance at a faster pace, hastening graphene's widespread industrial application.

<div align="center">**Future Research**</div>

A New Automated Exfoliation Device

First, a new device must be designed that can efficiently both exfoliate and transfer graphene. The efficacy of rolling exfoliation and stamping transfer have been supported by this study and literature (Mag-Isa, 2015), respectively, and therefore the combination of these two techniques in one device has promise. Rollers could exfoliate graphite on a continuous piece of Nitto tape which runs through and exits the device. SiO_2 could then be stamped onto the tape and secured in place, simulating the prolonged, flat contact from the manual method.

Discrepancy with Literature Results

Huang, et al., who originated O_2 plasma treatment and hotplate annealing in manual exfoliation, reported a "typical graphene size" of 350 x 500µm with their modified method. However, I could not replicate these large sizes with the roller or even with the manual method while replicating their O_2 plasma and 2-min 100°C hotplate anneal. My study confirmed that O_2 plasma and higher temperatures increased graphene size, but not to the degree they state in their results. Perhaps a different quality/size of HOPG was used, or a more aggressive O_2 plasma recipe, but these details were not published. This article was a motivation for the roller project, and it should be determined why there was a disparity in graphene size, either via correspondence with the authors or further experimentation.

Beyond Graphene

The new automated exfoliation device, along with changes to the method in accordance with Huang et al., could be used to produce 2D nanomaterials other than graphene. These include semiconducting transition metal dichalcogenides, such as WS_2 and $MoSe_2$, as well as hexagonal boron nitride, an insulator. Automated exfoliation also has use with unstable materials that require inert N_2 atmospheres, such as black phosphorus. Thus, automated exfoliation could be used to produce a wide range of 2D nanomaterials, each with unique properties and applications.

<div align="center">

Conclusion

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In this study, a novel roller device was used to explore the automated mechanical exfoliation of the 2D nanomaterial graphene. The roller was used to determine the effects of eight variables on graphene exfoliation: SiO_2 pretreatment with O_2 plasma, type of graphite, strength of adhesive tape, roller exfoliation time, roller transfer time, roller speed, inter-roller pressure, and atmospheric temperature. It was found that the preferred conditions were 120s O_2 plasma etching, Nitto tape, short exfoliation/transfer times, faster speed, and higher temperatures. The rollers efficiently exfoliated graphite, but inefficiently transferred flakes to the flat SiO_2 substrates. Therefore, the next-generation automated device should incorporate rolling exfoliation and stamping transfer to optimize production. With improved devices, researchers world-wide can use automated exfoliation to aid their experimentation, which will advance graphene's application in electronics, composite materials, desalination, and beyond.

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