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Evaluating the Scalability of the Sonication Method of Graphene Oxide Synthesis

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EVALUATING THE SCALABILITY OF THE SONICATION METHOD OF GRAPHENE OXIDE SYNTHESIS

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ABSTRACT

Graphene is a new material that was first isolated in 2004, and consists of one to a few atomic layers of carbon in a lattice sheet structure. Graphene has high tensile strength, high surface area, very low electrical resistance, and various other special properties that make it an excellent material for use in emerging technologies in the categories of electrical components, energy systems, and high strength applications. The production scale of graphene sheets and its variations is currently limited to laboratory use, with increasing research being conducted toward the development of manufacturing techniques of the material. We conducted experiments to analyze the scalability of graphene oxide synthesis through the sonication method, and hypothesized that increasing sonication volume and time would increase yield of graphene oxide. The synthesis of graphene oxide was scaled over 100-500mL while varying sonication from 60-180 minutes. The resulting product was analyzed for quantity by assessing the dry weight of each sonicated product. Product was to be assessed for definitive graphene oxide quality by Raman spectroscopy for both sheet size and purity of the product, but was unable to be completed due to machine failure as of this writing. Our data demonstrated that the production rate of graphene oxide is constant with increasing sonication volume, but decreases with increasing sonication time. The latter is typical of many chemical reactions and was expected of the synthesis, while the former indicates the feasibility of larger scale synthesis without trade-offs in production rate. Further research into the matter is needed at increasing volumes of sonication, and with greater repeatability of experiments.

INTRODUCTION

Graphene is a relatively new material, having been isolated for the first time in 2004 [1]. It consists of a few atomic layers of carbon atoms arranged in a hexagonal lattice, similar to the structure in the much more common graphite. Graphene with only one atomic layer is referred to as single layer graphene (SLG), and has superior characteristics to graphene with multiple layers, termed few layer graphene (FLG). Both categories of graphene possess many highly desirable traits which are uncommon in everyday materials.

Graphene's unique properties include high tensile strength, high proportional surface area, near zero electrical resistance, and high heat conductance [2]. These attributes make graphene a promising option for technologies currently in research and development. Possible areas of use for graphene include photovoltaic cells, display panels, supercapacitors, high strength composites, and various electrical devices [1], [2]. Due to its properties and broad applications, graphene promises to be an innovative force for technology in the foreseeable future, and consequently, the demand for high volume graphene manufacture is anticipated. Currently, graphene is made in laboratory environments in relatively small volumes on the order of milligrams to grams [3]. The complexities of its manufacturing processes make synthesis a challenge at scales needed for commercial products. Transferring graphene from the laboratory to the production floor is a crucial step in its adoption as an emerging technology. The goal of this research is to evaluate the scalability of graphene sheet synthesis through the use of liquid-phase sonication exfoliation. In the course of research, graphene synthesis was

conducted experimentally at various scales, and the resulting products were analyzed for quantity. Using the data from this research, the relationship between factors associated with the scaling of the synthesis process are evaluated to determine the efficacy of liquid-phase sonication exfoliation in large scale graphene synthesis.

REVIEW OF LITERATURE

Currently, there exist various methods of graphene synthesis, including liquid-phase sonication exfoliation, physical exfoliation, chemical vapor deposition (CVD), and various hybrid methods that combine elements of each [4]. The synthesis method chosen for this research is liquid-phase sonication exfoliation because it is cost effective, produces high quality graphene, and shows promise of meaningful scalability [4]. While other methods will not be attempted in order to retain focus in the research, they are discussed to provide a wider understanding of synthesis techniques being developed.

Synthesis Methods

Liquid-phase exfoliation methods remove graphene layers from larger particles of graphite while suspended in solution [2]. Prior to sonication, some methods include oxidizing graphite in order to expand the lattice structure and aid in the subsequent exfoliation [2], [5]. This produces a graphene oxide compound as opposed to a pure graphene material. After synthesis, graphene oxide may be reduced to graphene if it is desired, however it may not be necessary as graphene oxide shares many of graphene's unique properties [5]. Exfoliation is either achieved with the aid of an ultrasonic probe or with an ultrasonic bath. Both methods create ultrasonic waves but do so with

differing equipment: the former uses a vibrating probe that is lowered into the solution, the latter vibrates the entire container of liquid. In both cases ultrasonic waves are sent throughout the solution which cause cavitation bubbles to form, creating high shear stresses within the solution and causing graphene layers to shear off their parent graphite particles [6]. Present in the water solution is a surfactant which raises the surface energy of the solution to roughly that of the graphene sheets (~68 mJ/m^2) [3]. Various surfactants can be used so long as their concentration creates the appropriate overall surface energy for the solution. This prevents graphene sheets from coalescing and allows them to remain suspended in the solution. Others have used organic solvents such as NMP (N-methyl-2-pyrrolidone) which have equal surface energy in place of the water surfactant solution [3]. The drawbacks of an organic solvent include increased cost, difficulty in handling, and difficulty in evaporation compared to an aqueous solution [3]. During the sonication process, a portion of the ultrasonic energy is converted to heat, necessitating cooling of the solution over the course of the sonication [1]. Following sonication, both graphene sheets and remaining graphitic material are suspended in the solution. A centrifuge is used to settle the graphitic material to the bottom of the solution, leaving only graphene sheets in suspension as a result of their matching surface energy. The solution can then be decanted off and evaporated, leaving behind graphene product.

Physical exfoliation is a method similar in principle to liquid-phase sonication exfoliation, though regarded less in terms of production-level capability. This method uses physical motion, commonly in the form of a ball mill, to remove graphene layers

from graphite [7]. This is a sophistication of one of the first methods of obtaining FLGs, which involves mechanically removing FLG layers with scotch tape from graphite. While incredibly simple, this method produces very low quality and quantity graphene; drawbacks that extend to more sophisticated procedures of physical exfoliation [7]. The upside of this method is that it is inexpensive due to the simplistic tools involved and the use of few chemicals [7]. Despite this, the crystal structure of the graphene lattice struggles to stay intact during the mechanical exfoliation when compared to other methods [4].

CVD is a promising method that has been extensively researched, but has a high cost in both setup and operation [8]. In CVD, a carbon containing gas is heated until it reaches a temperature of 300°C to 1000°C, depending on the specific method, and is then deposited onto the surface of a metal or metal alloy substrate [9], [8]. A positive aspect of this method is that it is capable of being a reel-to-reel process, which are commonly used in industry and have promising scalability potential. However, CVD requires specialized equipment involved in the superheating and channeling of gases, which greatly raises the initial costs of the method [2], [9]. While this method may become more developed and economical in the future, it is not feasible for this research to investigate it.

Gap in Existing Research

While much research has been done in the field of liquid-phase sonication exfoliation of graphene, a gap exists that this research will attempt to fill. From the available literature, no specific study has been done on the relationship between

sonication time and volume in this specific method of graphene synthesis. These parameters of the synthesis are highly relevant to scalability, as they are likely to vary significantly between laboratory and production levels of synthesis. A significant portion of research previously done on this method of synthesis has focused on parameters not critical to scalability, such as graphite concentration [3], [6], surfactant concentration [3], thermal shocking effects [10], and vessel geometry [6]. Additionally, papers that investigate variable parameters of graphene synthesis typically do not include oxidation of graphite in their methods [1], [3], [10]. This research chooses to pursue an oxidative method as it has been found to increase yield as the expanded crystal lattice of graphite oxide can more easily be exfoliated [3], [5].

This research aims to fill a gap in existing research done by other studies. Arao and Kubouchi investigated the effects of sonication volume and its relation with graphite concentration in the initial solution for sonication [3]. They found that the most effective way to increase the amount of FLG produced is to raise the initial concentration of graphite, but not to exceed a critical concentration where efficiency decreases quickly [3]. The study found that this increase in graphite concentration was more critical to yield than an increase in sonication volume, which produced only a slight positive correlation with yield [3]. Another study by Gayathri et al. studied the effects of sonication time alone on the graphene product [1]. They concluded that yield increased linearly with sonication time, but did not reach yields as high as Arao and Kubouchi's study [1]. However, neither of these studies used oxidative methods for synthesis, meaning that the combined effects of variable sonication time and volume

with an oxidative synthesis method have not been determined. Direct comparison of key variables such as time and volume with respect to oxidative synthesis is critical to expanding our knowledge of graphene scalability.

METHODS

Experimental Trial Procedure

Graphene oxide was produced using 99.9% graphite powder, sold commercially as dry lubricant by Loudwolf Industrial & Scientific. The graphite was first oxidized by submersion in concentrated sulfuric acid for 8 hours to produce graphite oxide. Graphite oxide was made in 20g batches, each submerged in 100mL concentrated sulfuric acid. The solution was vacuum filtered using a glass fiber filter, and the residue dried in a crucible on a hot plate until visibly dry. The graphite oxide was then placed in a tall-form beaker as the sonication vessel. The concentration of graphite oxide used in sonication was 20g/L. The planned total solution volumes used for sonication were 100, 200, 500, and 1000mL. The tall-form beakers used were of volumes 200, 500, 1000, and 2000mL for the different respective sonication volumes. Water was added to the graphite oxide up to the desired solution volume, and Triton X-100 surfactant was added at a concentration of 0.5g/L. Aluminum foil was used around the rim of the beaker to keep solution from splashing out during sonication. Sonication of each solution was then performed with a VirTis VirSonic 475 sonication probe at full power for varying times of 60, 120, 180, and 240min. With these four varying sonication times and the four levels of sonication volume, a total of sixteen trials were completed. The

sonication probe was placed 1cm into the solution, in the center of the beaker. An ice bath was used during sonication to keep the solution cool and the probe from overheating. The ice bath was refilled as needed during each sonication process. From the sonicated solution, 100mL was pipetted into two 50mL centrifuge tubes and centrifuged at 3220 RCF for 30 minutes. This centrifuge setting was picked as specific information could not be found in other studies, so the highest setting on the centrifuge was used. Preliminary testing indicated that this setting was sufficient to sediment the remaining graphitic material on the bottom of the tube. From each tube, the top 40mL of solution was decanted off (for a total of 80mL from each trial) and dried in an evaporating dish with a hot plate at 120°C until visibly dry. Initially each 80mL sample had the appearance of clear liquid, however brown to black powder residue resulted upon evaporation.

Analysis Methods

Once the final graphene oxide was dried, the mass was weighed and recorded. Values of percent yield, yield per liter, and rate of production were calculated and compared for each run. It was assumed that the Triton X surfactant was evenly distributed in the sonicated solution, did not evaporate off, and therefore contributed to the final dried mass [3]. To confirm this assumption, three tests were done where a 100mL solution of water, graphite oxide, and Triton X were centrifuged without performing sonication. The solutions were then dried as the sonicated trials were, and the residue weighed.

Samples from each experimental run were collected and sent to Dr. Gamini Sumanasekera at the University of Louisville for Raman spectroscopic analysis. From Raman spectroscopy results, conclusions about the graphene oxide's quality can be made. When graphene is analyzed with this type of spectroscopy, it produces distinctive bands named the 'D', 'G', and '2D' bands. The ratio of the intensities of the 'D' and 'G' bands in the spectra can be calculated to find the relative quality of the graphene structure: a smaller ratio indicates fewer defects [3]. The '2D' band can also be analyzed for symmetry and peak intensity, both of which indicate fewer layers of graphene oxide with increasing value [3].

Process Difficulties

During the experimental testing phase of this research, parameters outside of our control caused portions of the planned methods to remain incomplete. In order to sonicate the larger volumes of the 500mL and 1000mL solutions, a larger probe horn was purchased (Branson 620-001-156, Emerson Industrial Automation, used). Unfortunately, the new probe horn caused the sonication machine to overheat and was thereafter inoperable. This reduced the number of completed trials to 6 instead of the

Table 1. Completed experimental trials by experimental factor level. Due to difficulties previously discussed, not all planned experimental trials could be completed. This table shows the trials that were successfully completed, identified by their specific combination of experimental factor levels.

Sonication Time Factor (minutes)	Sonication Volume Factor (mL)			
	100	200	500	1000
0 (Control)	Completed	N/A	N/A	N/A
60	Completed	Completed	-	-
120	Completed	Completed	Completed	-
180	Completed	-	-	-
240	-	-	-	-

planned 16, thus not all sonication times and volumes were tested. Table 1 shows the factor levels of the experimental trials that were completed. Once samples of each completed trial were sent to Dr. Sumanasekera for analysis, it was made known that the Raman spectroscopy machine at the University of Louisville was non-operational and in need of repairs. As of the writing of this thesis, the results of the Raman spectroscopy analysis have not been received back from Dr. Sumanasekera. Despite these setbacks, useful conclusions about the scalability of this method for the synthesis of graphene can be inferred from the data that were collected.

RESULTS

In order to determine the scalability of graphene synthesis by liquid-phase sonication exfoliation, we utilized a direct comparison approach assessing both volume and time of oxidized graphite. Total product collected from varying sonication time and volume are shown in Table 2. The product collected is an adjusted value that reflects the removal of the remaining Triton X surfactant. As 0.5 g/L Triton X was used in each trial, 0.04g would be present in each decanted 80mL sample taken and was subtracted accordingly from the measured dry weight. This assumption was confirmed by assessment of un-sonicated solutions. The three un-sonicated controls of 100mL graphite oxide solution yielded residue masses of 0.033, 0.032, and 0.035 grams, attributed to the non-sedimenting and non-evaporating Triton X. Since the accurate collection of such small masses of residue was difficult, it seems that the true value of

residue was in fact the calculated 0.04g, making 0.04g the appropriate amount to subtract from the sonicated residue to calculate graphene oxide mass.

The extrapolated product in Table 2 indicates the expected total yield had the entire solution (100, 200, or 500mL) been processed as the product collected from the 80mL portion. The percent yield reflects the percentage of graphene oxide obtained from the original graphite oxide. The rate of production shows the speed of the exfoliation process and is a key indicator of scalability of the synthesis. It should be noted that this is a calculated rate from the entire length of the sonication. The instantaneous rate of production likely varied with time during the sonication process, and will be discussed further below with the varying lengths of time, helping to determine the time variance of the rate of production.

Table 2. Results of the experimental trials of graphene oxide synthesis. In this table, the product collected is the raw dried weight measured from each trial, the extrapolated product is the calculated product if the entire volume of the trial was centrifuged and dried, the percent yield was calculated using the beginning weight of graphite oxide used, and the rate of production was calculated using the volume and time of each trial.

Sonication Volume (mL)	Sonication Time (minutes)	Product Collected (grams)	Extrapolated Product (grams)	Percent Yield (%)	Product Concentration (grams · L^{-1})	Rate of Production (grams · L^{-1} · min^{-1})
100	60	0.335	0.419	20.9	4.19	0.0698
100	120	0.422	0.528	26.4	5.28	0.0440
100	180	0.261	0.326	16.3	3.26	0.0181
200	60	0.234	0.585	14.6	2.93	0.0488
200	120	0.225	0.563	14.1	2.81	0.0234
500	120	0.370	2.313	23.1	4.63	0.0385

Due to extenuating circumstances, the Raman spectroscopy was unable to be completed for the synthesized samples. Consequently, the purity of the product created remains unknown. However, evidence suggesting the product primarily

contained graphene oxide includes the results of the un-sonicated control samples, as well as the fact that prior to drying, the solution appeared clear without particles. Any significant graphitic material should have precipitated to the bottom of the centrifuge tubes, leaving only graphene oxide invisibly in suspension in the solution. Despite this, Arao and Kubouchi synthesized concentrations of FLGs up to 1.8g/L in their probe sonication research, which is considerably less than the maximum concentration produced in this research [3]. This disparity in yield leads us to believe that some of the graphite oxide in our research may have been exfoliated into particles small enough to remain in suspension but too large to be considered an FLG, an explanation proposed by Dr. Sumanasekera [5]. For the analysis of these results, it will be assumed that a significant portion of the dry products created are graphene oxide, and that the dry weight collected is proportional to the true amount of graphene oxide produced.

DISCUSSION

The objective of this research was to determine the scalability of graphene oxide synthesis. The calculated values were chosen to show how the parameters tested may affect the synthesis under differing conditions. The low number of trials completed is a weakness of this research, and reduces the weight of subsequent conclusions. Ideally, and as a suggestion for future research, this research would have completed all 16 combinations of factor levels as originally proposed, and performed repeat trials under the same conditions for greater confidence. Additionally, greater volumes would also

be a valuable addition to further research, but would require additional lab equipment such as much larger beakers or vessels and larger sonication horns.

Upon initial review of the raw weights collected, any trends in data from sonication volume (Figure 1) and time (Figure 2) are difficult to assess due to low experimental number. The percent yield was also included in these graphs as it corresponds directly to the dry weight collected. With a greater number of trials, a trend may have emerged, but with the data collected, none are apparent. The concentrations achieved in this research was higher than those of other studies such as Arao and Kubouchi, and Gayathri et al. [1], [3]. In reference to Arao and Kubouchi's research (who achieved a concentration of 1.8g/L compared to our maximum of 5.28g/L), the discrepancy may be due to the use of oxidation and resulting graphene oxide product [3]. This cannot be definitively stated, however, since it is not known how much of the product is actually FLG. Comparing to Gayathri et al., their lower

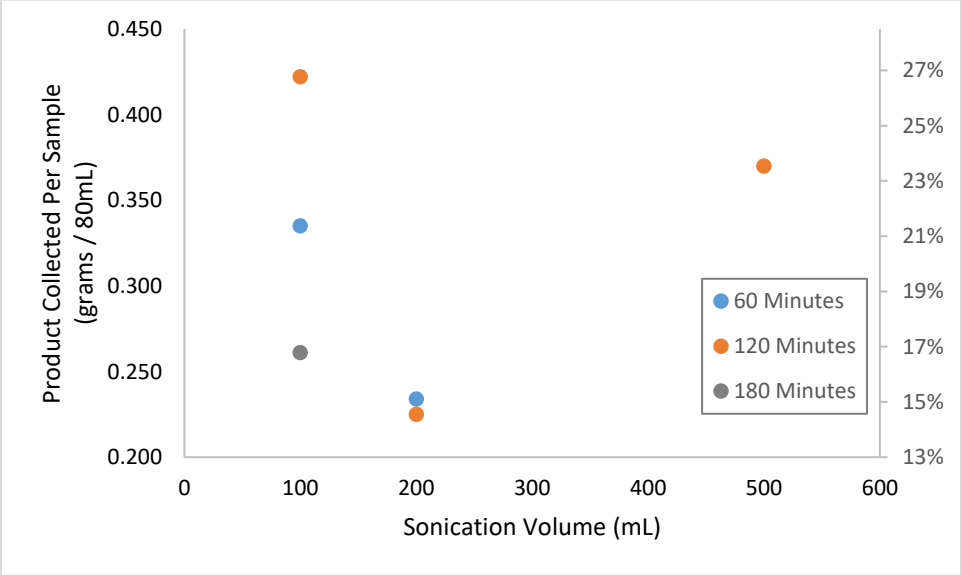

Figure 1. Product collected per sample and percent yield by sonication volume. The amount of product collected per sample is the raw measured dry weight. The percent yield was calculated using the beginning weight of graphite oxide used in each trial.

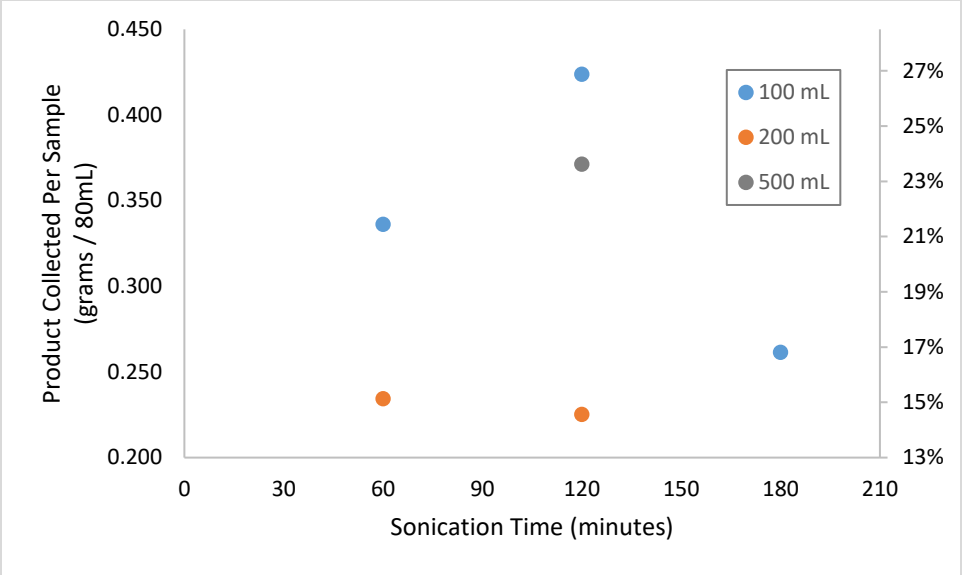

Figure 2. Product collected per sample and percent yield by sonication time. The same data are shown here as in Fig.1, but graphed by their time factor levels.

concentration of 6.6mg/L can be explained by their lower power sonication probe: 100W compared to our 475W [1]. The probe used in Arao and Kubouchi's study was rated 600W [3]. Additionally, Gayathri et al. cannot be compared to this research apples to apples as they used a differing method of sonication that included a substrate for the graphene film [1].

By taking the previous data and controlling for volume by dividing by the sonication volume of each trial, the overall rate of production was found (Figures 3 and 4). These results provide more useful data for conclusions to be made. Graphing the overall rate against sonication volume, shown in Figure 3, there appears to be no trend. This is actually a positive result for the synthesis method as one may have suspected the rate of production to drop as a result of increasing volume, and subsequent increase on material needing to be exfoliated. The lack of a declining production rate indicates that the process may expandable to larger volumes without compromising the speed of the

method. Again, a greater number of trials would be helpful to solidify this conclusion, particularly since there is a sizeable spread of rates within trials of the same volume amount.

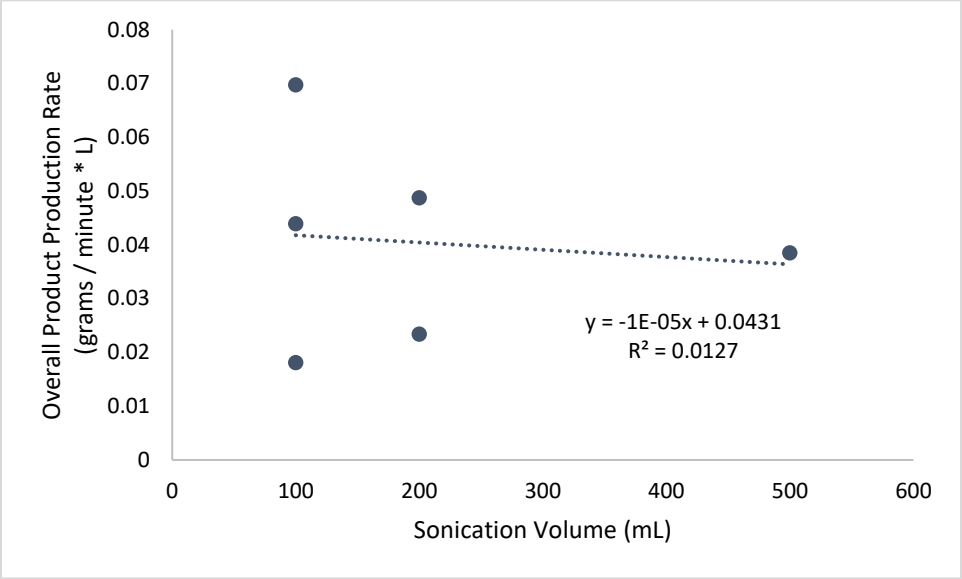

Figure 3. Overall product production rate by sonication volume. This graph shows the overall production rate of graphene oxide is not significantly influenced by sonication volume.

When viewed as a function of sonication time, there is a negative relationship between production rate and sonication time (Figure 4). This suggests that there are diminishing returns to running the sonication for longer periods of time, and that a majority of the work of exfoliating the graphene sheets may be done relatively early in the sonication process. It seems that the instantaneous rate of production would approach zero as sonication time increases. These results are typical of most chemical reactions, except in cases of thermally driven exothermic reactions. These results contradict the findings of Gayathri et al. which identified a positive linear relationship between time and yield [1]. We believe this is due to the lower power sonication probe used in their research (compared to ours and that used in Arao and Kubouchi [3])

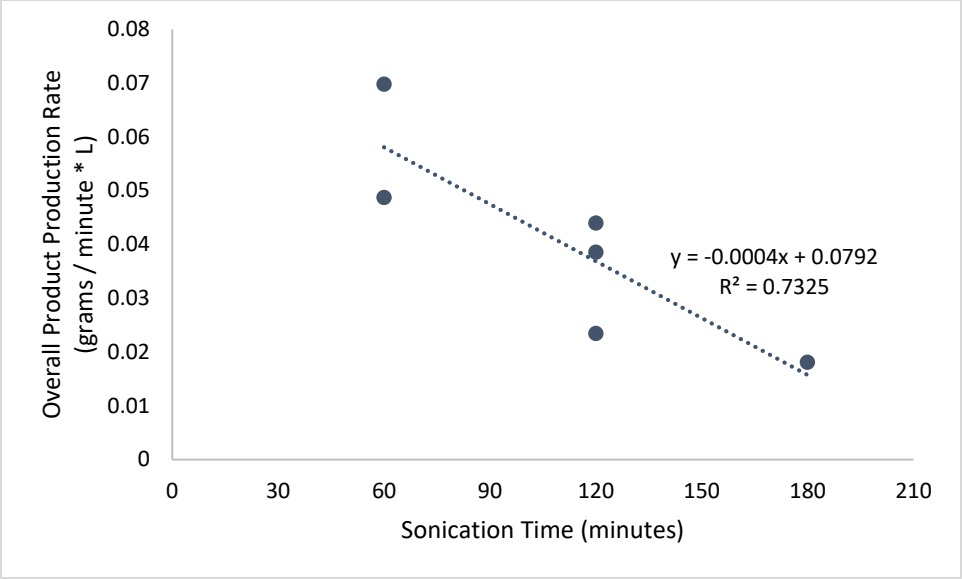

Figure 4. Overall product production rate by sonication time. This graph suggests a negative relationship between the overall production rate of graphene oxide and the sonication time.

meaning that their synthesis may not have reached a point of significant diminishing returns. Whether or not all of the graphite oxide would eventually be exfoliated to graphene oxide is uncertain. The application of this data would be that there is an ideal time that a sonication process should run to produce the most graphene oxide without needlessly lengthening the process. In an industrial setting, a recycle system might be implemented to capture the unexfoliated graphite oxide after the process and direct it back into the sonication process alongside fresh material.

The final mode of analyzing the data is shown in Figure 5 where the extrapolated product is compared to the sonication volume used. The results of this graph logically follow from the findings that production rate remains constant with increasing volume. Because the rate of production appears to remain constant despite increases in volume, an increased volume will directly lead to higher yields, as the concentration of graphite oxide was held constant. The combination of rate data and total extrapolated product

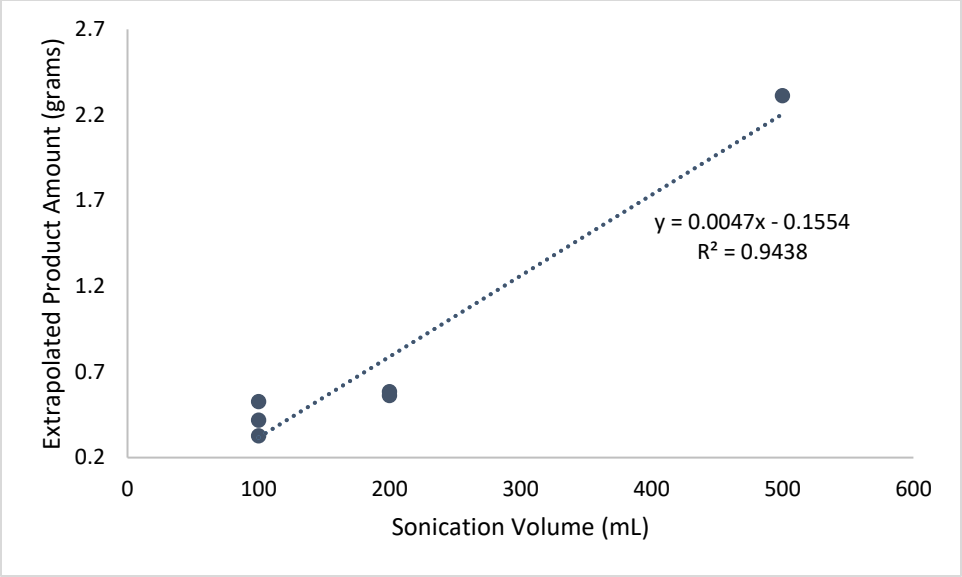

Figure 5. Extrapolated product amount by sonication volume. This graph shows the collected dry weight extrapolated out as though the entire sonication volume was centrifuged and dried. The approximately direct relationship between these values agrees with the previous conclusion that the overall production rate is unaffected by sonication volume.

data give evidence that larger volumes of sonication are feasible for synthesis processes. This makes liquid sonication an attractive method for graphene oxide production. In other methods, scaling up may require specialty or complex equipment to be obtained at larger sizes. However for liquid-phase sonication the major process component appears to scale with the simple substitution of a larger vessel. More research is recommended to determine if these relationships continue to hold for increasing scales that approach production levels.

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