Exfoliation of Hexagonal Boron Nitride Through Sonication and Centrifugation

By James Nebeker

Advisor: Hannes Schniepp

Senior Research Coordinator: Henry Krakauer

May 2012

A thesis submitted in partial fulfillment of the requirements for the degree of
Bachelor of Science in Physics from the College of William and Mary

Abstract

Boron Nitride is an interesting material, a structural analog of graphene that has been shown to have comparable strength and toughness while exhibiting several unique properties that make it preferable to graphene in some ways. Unlike graphene, there is no established method for obtaining large amounts of single-layered Boron Nitride. Given its unique properties, there is much to gain from establishing an efficient process that yields such material. The objective of this project is to move toward creating such a process, and to make it as efficient and productive as possible. Borrowing from successful techniques for graphene separation, we hope to find a combination that will successfully separate a high number of single-layered Boron Nitride sheets. The material obtained from such a process would have exciting and significant applications in materials science and physics.

Table of Contents

List of Figures

Introduction

Boron Nitride is a fascinating material due to its structural similarities to graphite and its well-known allotrope, graphene. However, it is the significant differences that Boron Nitride has from this carbon system, particularly in its hexagonal form, that make it a notable material for future applications in a variety of fields.[1,4,5,6] Additionally, Boron Nitride is an underrepresented material in comparison to its famous analog, graphene; for the number of publications relating to Boron Nitride is remarkably smaller than those pertaining to graphene.[1] In the literature that has been published, others have exfoliated Hexagonal Boron Nitride (h-BN) to obtain Boron Nitride Nanosheets (BNNSs) using a variety of methods with the goal of recreating what has previously been accomplished with graphene.[1,2,3,9] In this research project, we use a combination of previous techniques, sonication and centrifugation along with chemical processes, in an attempt to exfoliate h-BN. Using atomic force microscopy for analysis to evaluate the changing of different factors of the experiment (e.g., sonication duration/intensity, centrifugation speed), we hope to obtain an ideal process that maximizes yield of mono-layered BNNSs of large lateral size, which can be used in numerous applications in physics and materials science.

Boron and nitrogen atoms behave similarly to carbon when bonded with each other to form Boron Nitride, exhibiting many similar structures as carbon only with alternating B and N atoms instead of C atoms.[4] Because of this, there are many forms of Boron Nitride that coincide with carbon structures and have a variety of properties and functions. Hexagonal Boron Nitride (h-BN) is a common form of BN that has a similar configuration to graphite. Like graphite, h-BN consists of hexagonal layers of covalently bonded B and N (sp^2–hybridization) stacked on top of each other, with adjacent layers weakly held together by van der Waals forces and an interlayer separation of ~0.33nm.[2] Analogous to graphene as a single atomic layer of graphite, Boron Nitride nanosheets (BNNSs) consist of mono-layered planes of h-BN.[1] BNNSs are obtained by overcoming the forces of attraction between neighboring layers of h-BN to break apart the stacked sheets. This process is called exfoliation and its successful achievement would be critical for many interesting applications.

BNNSs exhibit properties similar to those notable in graphene, like high strength and thermal conductivity.[3] However, BN exhibits some marked differences from graphite that contribute to the material's significance. First, BN is remarkably stable both thermally and chemically.[1] In addition, h-BN is an electrical insulator with a large band gap (4—6 eV),[2] due to a higher electronegativity of nitrogen; another consequence of this is that BN is white in color.[4] The downside to its chemical stability is that h-BN is more difficult to exfoliate than graphite; this is because some proven methods of exfoliation used for graphite, mainly chemical techniques, seem to have less effect on the h-BN system.

Due to its beneficial properties, h-BN has many applications. Traditionally, h-BN has been used as an industrial lubricant, specialized for high temperature conditions due to its thermochemical stability and the ease with which layers of h-BN are ably to slide freely past one another.[4] Additionally, h-BN in bulk form has been used in cosmetics and as a machined ceramic in industrial parts.[5] More exciting are the applications of BNNSs, which take advantage of h-BN's properties on a nano scale. First, due to their high mechanical strength, BNNSs could be useful for polymer reinforcement. BNNSs have already been shown to increase the elastic modulus and strength of thin polymeric films.[1] Such polymers would be useful in high temperature conditions and can also be used by NASA to provide space radiation shielding for future spacecraft.[6] Since h-BN is an electrical insulator, BNNSs can also be used as a non-conducting substrate in electrical applications such as nanoscale electronic components.[1]

The objective of this project was to discover a process that yields a large amount of mono-layered sheets of Boron Nitride of significant lateral size, while minimizing the amount of material still in bulk layered form. Currently, limited methods for exfoliation of h-BN to obtain BNNSs have been published, but there exists no process for high-yield, bulk exfoliation of h-BN. In an attempt to find such a process, we have borrowed some methods from previous literature that have shown success in exfoliating graphite to obtain large amount of graphene. For example, methods such as chemical exfoliation[2,7,13] and sonication[1,2,3,8,9,14] have been shown to exfoliate h-BN to some degree of success.

Following this example, our first basic method entailed the combination of sonication and centrifugation to treat h-BN powder. Sonication is a process in which the material is exposed to a bombardment of sound waves, which are transferred to the target through a solution. Repeated exposure to the energy from the sound waves overcomes the weak forces of attraction between neighboring h-BN sheets, causing the sheets to break apart.[3] Ideally, the stacks of h-BN sheets will break apart into single layers and the solution will largely contain BNNSs after sonication. Since the ideal case of complete exfoliation to mono-layered material is not always present, we use centrifugation to separate out the thinner and smaller sheets of h-BN from the larger stacks that remain un-exfoliated.

In addition to this basic method, we tested other means of h-BN exfoliation that have seen much success in graphene production. The first of these consisted of chemical exfoliation of raw h-BN powder prior to sonication and centrifugation. We used the Hummers reaction, which has been known to aid in the exfoliation of graphite.[10] In this reaction, strong acids are used to oxidize the material being treated.[10] In the case of graphite, the oxidation leads to an increase in the separation distance between layers of graphite which lessens the forces of attraction between layers and encourages exfoliation.[11] We hope to have similar success with this reaction in the treatment of h-BN, and will compare raw and treated powder to see if there is any significant effect on exfoliation from this process.

Another approach we tested with the hopes of improving the exfoliation process was the choice of solvent used to form the solution containing h-BN to be sonicated and centrifuged. The solvent plays an important role in aiding exfoliation and many different common solvents have been shown to be more successful than other in exfoliating h-BN.[12] We mainly utilized the organic solvent Dimethylformamide (DMF), which has proven useful in previous exfoliation experiments of h-BN.[1,2,3,13] DMF is a strong polar solvent and is useful because its polar molecules interact with layers of h-BN which lead to easier exfoliation of BNNSs.[3] We then compared the effectiveness of DMF with another solvent, Isopropanol (IPA). IPA is very common and has been shown to be quite effective in aiding h-BN exfoliation.[12,14] Using these

3

experiments, we can determine what is most effective in exfoliating h-BN to obtain large

quantities of BNNSs and, in combination, will lead to the most efficient and productive process for

Boron Nitride exfoliation.

Experimental

Sample Preparation and Atomic Force Microscopy

In order to study and classify the effectiveness of the exfoliation process, we use atomic force microscopy (AFM) to visualize any BNNSs or larger stacks of h-BN obtained during exfoliation. In this project, Silicon Nitride (SiNi) AFM tips were used with contact mode being the primary method of scanning. Semi-contact (tapping) mode was also used sparingly to take advantage of its phase signal, which can help differentiate different materials found in a scan.[15]

To scan any treated h-BN, a sample must be prepared and spin coated on a substrate. In this project, AFM samples were prepared by pipetting the treated h-BN in solution onto a substrate of mica. The solution was spin coated on the mica substrate at 2000 RPM for three minutes. Spin coating is used to help ensure an even distribution of material on the substrate, making scanning and characterization easier.

Sonication and Centrifugation

This is the central process in this research and these steps were used in some variation all experiments. We first combined h-BN powder and DMF (5 mg/mL) and sonicated this solution for 2 hours using a tip sonicator. The solution was surrounded by an ice bath to keep its temperature down as much heat is created during prolonged sonication. Next, three samples of the sonicated solution were immediately centrifuged at three different values of relative centrifugal force (4000, 7000, and 10 000 × g) for ten minutes each. Relative centrifugal force (RCF) is the acceleration that the sample is under during centrifugation and is given by the following equation:

$$RCF = \frac{r\omega^2}{g}$$

where r is the radius of the centrifuge, ω is the rotational speed, and g is the acceleration due to earth's gravity. RCF is given in multiples of *"g"* and is a more beneficial measurement than rotational speed (RPM) because it takes into account the radius of the centrifuge, which may be different between devices. It is also easy to switch back and forth between values of RCF and

RPM, given the radius of the centrifuge. After centrifugation, portions of the supernatant of these samples were prepared for AFM scanning using the process outlined previously. The purpose of this experiment was to study the effect of RCF value on the quality of material retrieved. We hope to find an ideal value of RCF for future experimentation that sufficiently removes large stacks of h-BN while not excluding thinner sheets that may have large lateral size.

The next experiment consisted of the same basic process as before but with an extended time of sonication. We hope that longer exposure to sound waves will allow more sheets of h-BN to break off into BNNSs. Here, a 5 mg/mL solution of h-BN powder in DMF was prepared and sonicated for 7 hours and subsequently centrifuged at 10 000 $\times g$ for 10 minutes. With comparison between this experiment and the first, we should be able to conclude which period of sonication is more effective in exfoliating h-BN.

Raw vs. Hummers Boron Nitride

The Hummers method is a powerful reaction used to chemically exfoliate materials. Raw h-BN powder was treated with the reaction and the resultant powder was stored for use in experiments. This Hummers reacted powder was used for the first experiments outlined in the previous section. We hope that the Hummers reaction has a significant effect on Boron Nitride despite it being resistant to chemical treatment. To see the effect of the chemical exfoliation, we repeated the first experiment with raw h-BN powder that had not been treated with the Hummers method. Comparing the two experiments should give insight into whether the Hummers reaction leads to thinner BNNSs in larger quantities, or the chemical stability of Boron Nitride prevents the Hummers reaction from having significant effect.

Change of Solvent

Choice of solvent used to create a solution of h-BN for sonication has a powerful effect on the result of the experiment and its effectiveness. DMF was used primarily during the first experiments due to its success in previous literature as a solvent for h-BN exfoliation. We tested another solvent, IPA, to see if there was any major difference in the amount of BNNSs retrieved

6

during sonication and centrifugation. First, a 5 mg/mL solution of h-BN powder and DMF was sonicated for 2 hours on ice. This sample was then centrifuged at 7000 $\times g$ for 10 minutes. Next, a similar solution of h-BN powder and IPA was sonicated and centrifuged under identical conditions. We hope a comparison of the two samples using AFM imaging will reveal if there is a significant benefit to either solvent or if their effect on the exfoliation of h-BN is too similar to have a large significance.

Image Analysis and Characterization

The results in this project come in the form of AFM images. Images are useful for visualizing results and provide a concrete, simple way to see what an experiment has yielded. Using images we can identify the presence of single-layer BNNSs and larger stacks of h-BN. The downside to a reliance on images as results comes during large-scale comparison and trying to make scientific conclusions. Relying on judgment to determine which set of scans looks to have thinner sheets is very subjective and qualitative, which doesn't warrant a substantive conclusion. To remedy this quandary, we have attempted to use a couple of programs to convert the data collected in each scan into quantitative results. Our goal is to calculate values of average thickness and lateral size of h-BN sheets found during scanning. A comparison of these numbers, if they are valid, will lead to a more conclusive comparison of different exfoliation methods.

First, an image-processing program called ImageJ, known for analysis of microscope samples, was used to calculate and average the area of all h-BN sheets scanned. More difficult was the calculation of height data. AFM raw data cannot be loaded into ImageJ so use of its powerful features to automatically detect and measure each sheet was not an option. Instead, an AFM data processing program called ScanHaSee was used. Without the capability of identifying each sheet separately the only option was to export the average height of every pixel in each scan and divide this by the area fraction of h-BN sheets in each scan (calculated by ImageJ). This division by the fraction of the total area that contains h-BN removes the zero height values

from the substrate. Unfortunately, this only gives an average height of each pixel of h-BN not each sheet, which would be the ideal case. Still, this allows us to make a somewhat quantitative conclusion about different exfoliation processes.

Results and Discussion

Centrifuge Speed Testing

Our first goal was to test the influence of the centrifuge speed on the size distribution of the obtained sheets of h-BN. Relative centrifugal force values of 4000, 7000, and 10 000 $\times g$ were tested and scanned as described above. Sample images for each RCF value are given in figures 1,3,5. Cross-sections of certain sheets of h-BN are shown in figures 2,4,6. A summary of the results from average sheet height and average sheet size analysis is shown in Table 1.
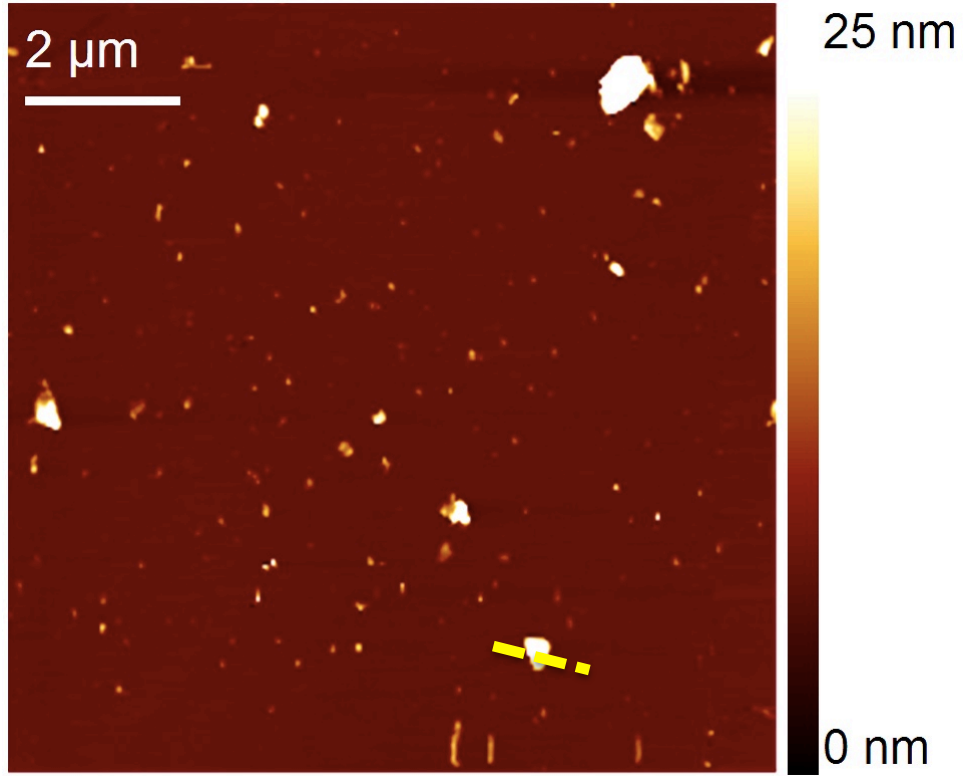
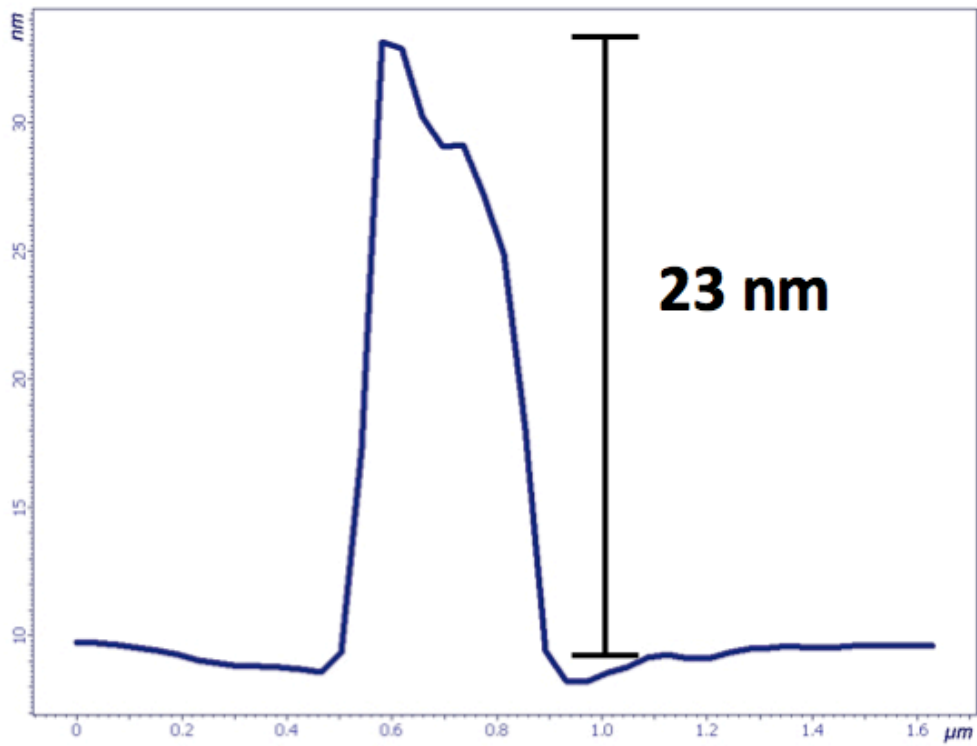**Figure 1:** Contact-mode AFM image of h-BN sheets centrifuged at 4000 × *g*

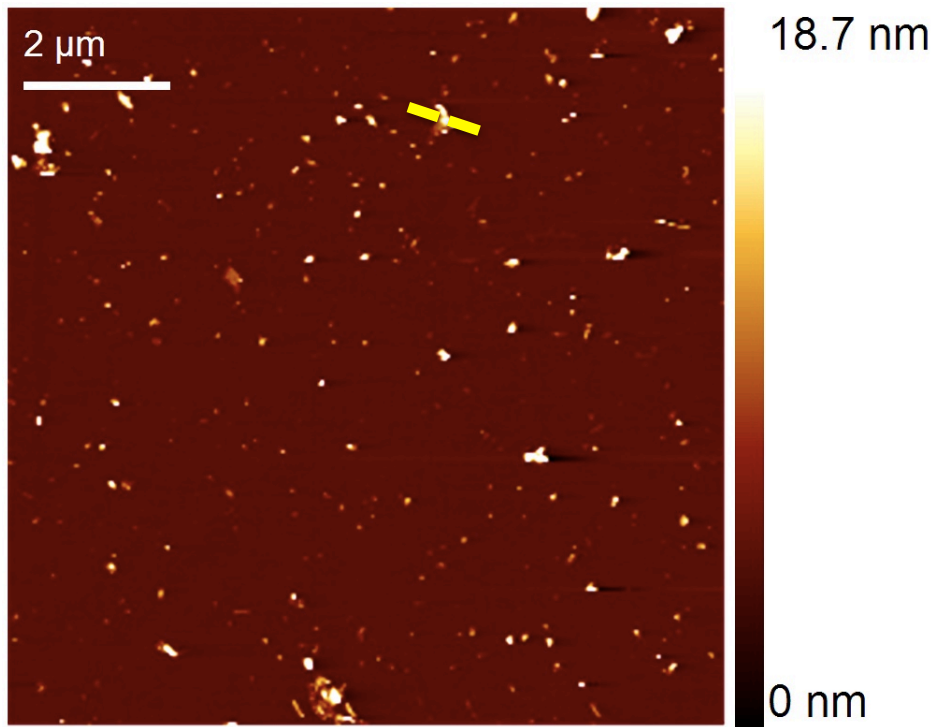**Figure 2:** Height cross-section of h-BN sheet marked in Fig. 1

Figure 3: Contact-mode AFM image of h-BN sheets centrifuged at 7000 × g
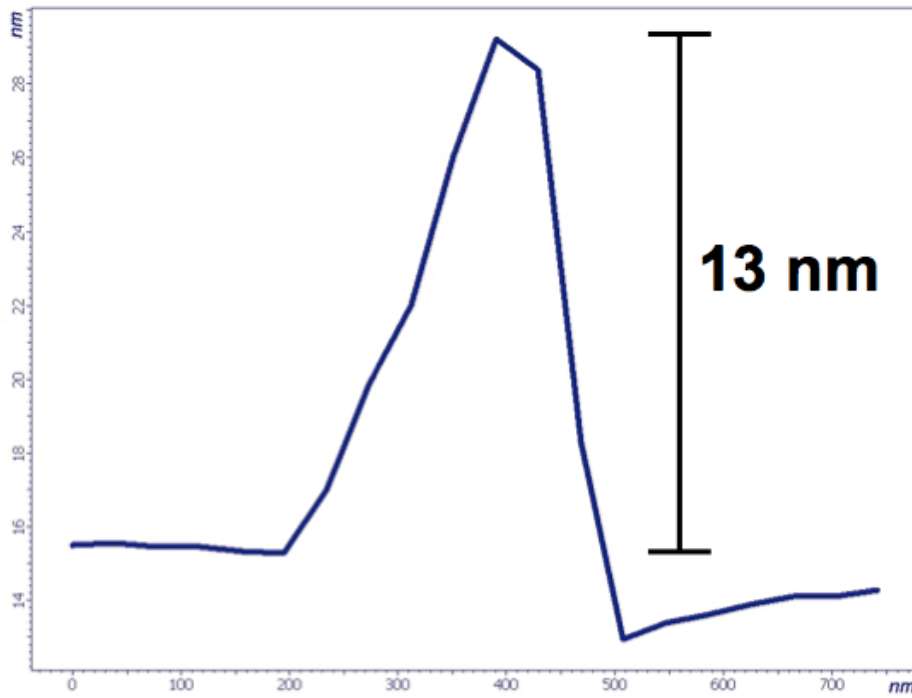

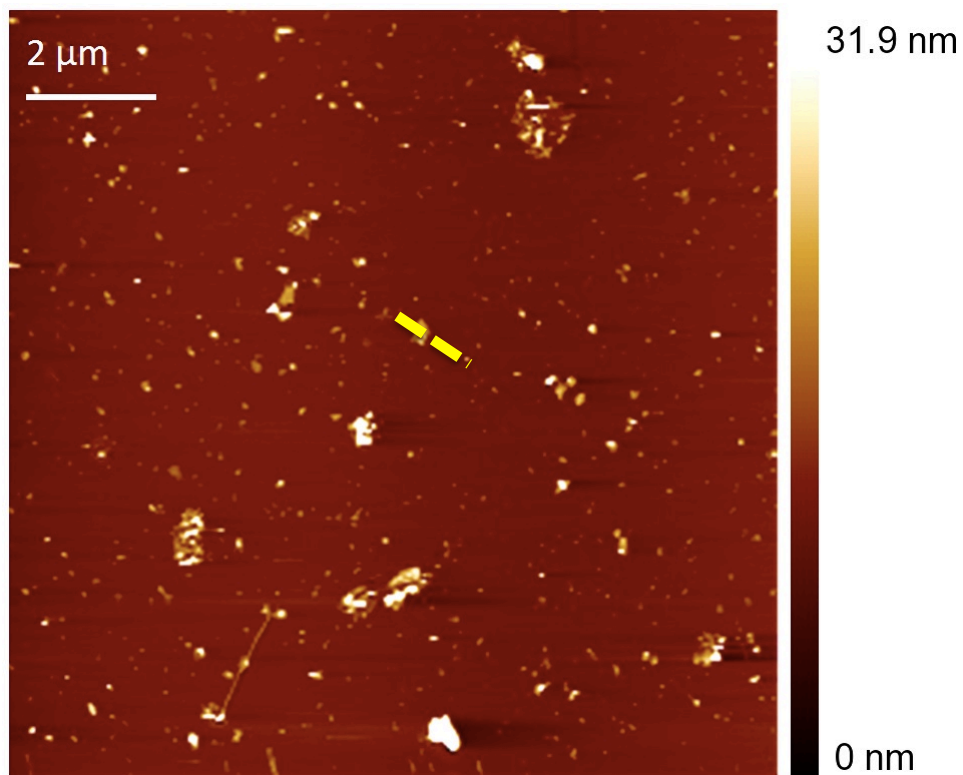**Figure 4:** Height cross-section of h-BN sheet marked in Fig. 3

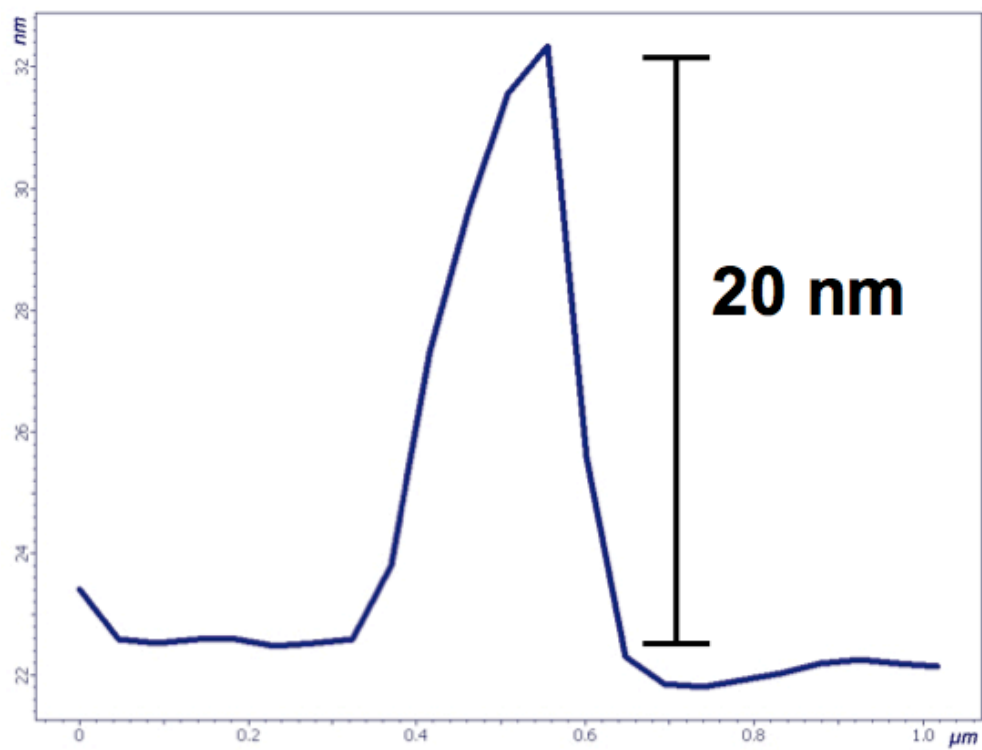**Figure 5:** Contact-mode AFM image of h-BN sheets centrifuged at 10 000 × *g*

Figure 6: Height cross-section of h-BN sheet marked in Fig. 5

RCF Value	Avg. Sheet Height	Avg. Sheet Radius	Area Fraction
4000 $\times$ *g*	9 nm	130 nm	5.7%
7000 $\times$ *g*	8 nm	79 nm	1.9%
10000 $\times$ *g*	10 nm	86 nm	3.0%

Table 1: Results from Avg. Sheet Height/Size Analysis

Figure 1 shows an array of h-BN material on top of a mica substrate from the 4000 $\times$ *g* experiment. The level substrate is shown in red while the height of the Boron Nitride sheets are seen in comparison to the color scale on the right. Using the scale bar in the top left of the image we can get an idea for the lateral size of these sheets, with the majority of them being less than 100 nm in size. An ideal value of lateral size would be upwards of 1 μm and this is true of a few sheets in figure 1, but a caveat of these sheets of large lateral size is their undesirable thickness. This is seen in the cross section of one of these sheets shown in figure 2; it shows a sheet height of 23 nm, which is far greater than the 1 nm thickness that indicates monolayer thickness.

Figure 3 gives a similar distribution of Boron Nitride sheets, this time from the 7000 $\times$ *g* experiment. Once again the majority of sheets are less than 100 nm in lateral size, but in this particular image it appears that most material has smaller thickness than the sheets in figure 1. This is supported in figure 4, which shows a sheet thickness of 13 nm for a particular sheet of large lateral size.

Figure 5 shows h-BN sheets exfoliated and centrifuged at 10 000 $\times$ *g* and dispersed on a mica substrate. This image shows a greater amount of large sized h-BN sheets than figures 1 and 3, but the cross section in figure 6 also indicates a large thickness of these sheets (20 nm). Also present in figure 5 is a more dense distribution of Boron Nitride material compared to other scans. This is important when considering the efficiency of an exfoliation process as a greater number of sheets means more material has been successfully exfoliated.

Table 1 shows our attempt to quantize the data from these experiments to make a more concrete conclusion on the effect of RCF value on quality of material obtained. We calculated

values of average sheet size and height using the methods outlined previously. Unfortunately, the uncertainty in the values of average sheet height is high due to the imprecise method of data collection, where this value is actually the average height of each pixel of h-BN in scanned images, not each individual sheet as a whole.

We expected to see a larger number of thin sheets and smaller number of thick sheets as RCF value increases, as a larger centrifugal force will better separate out a centrifuged sample. Instead, the data show that there is no discernable difference in the quality of material obtained from the different centrifuge speeds. The values of average sheet height from the three experiments are very similar and well within each other's margin of error (which could not be calculated but is estimated at $\pm$ 5 nm). Therefore, no absolute conclusion can be made about the most effective RCF value for obtaining BNNSs.

Also seen in this analysis is that the largest area fraction, or percent of the substrate covered by h-BN material, occurs for the smallest RCF value. Perhaps too large of an RCF value separates out an excess of h-BN leading to less overall h-BN material being present. In addition, it is possible that the lowest RCF value is successful in separating out the thinnest sheets and further increasing the RCF simply coincides with less of this material being retained. While a concrete conclusion cannot be made, these experiments have still shown that the process has successfully exfoliated h-BN sheets to a thickness of several nanometers in relatively large quantities.

Extended Sonication

Extended sonication of 7 hours was tested as outlined above. Figures 7 and 8 show two scans of the resultant h-BN after this treatment.
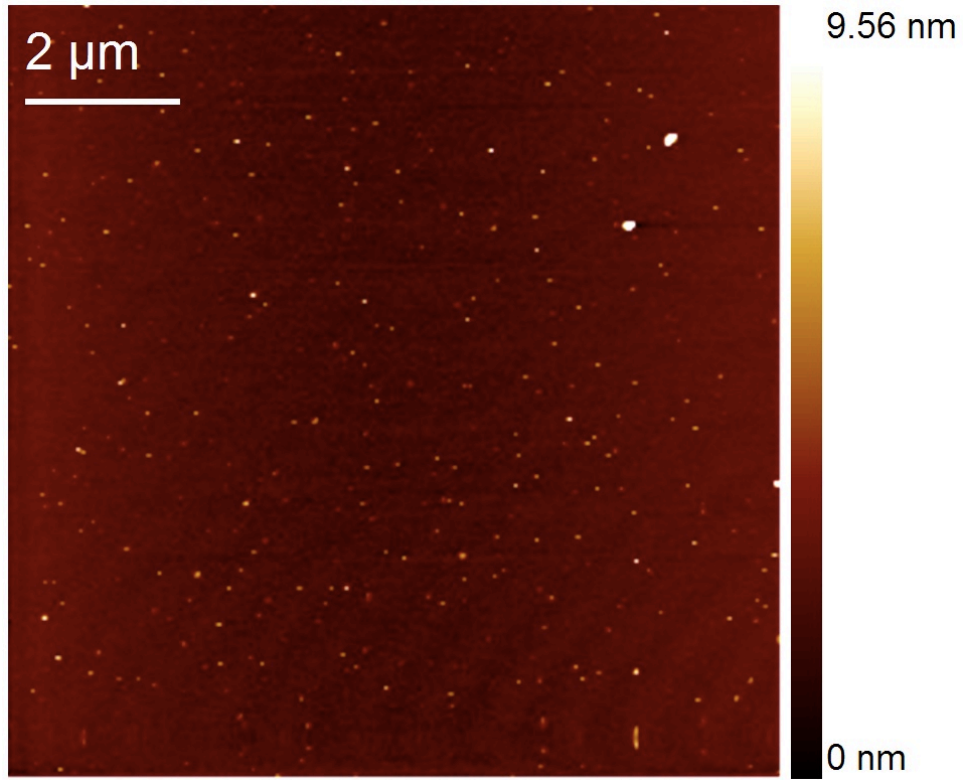
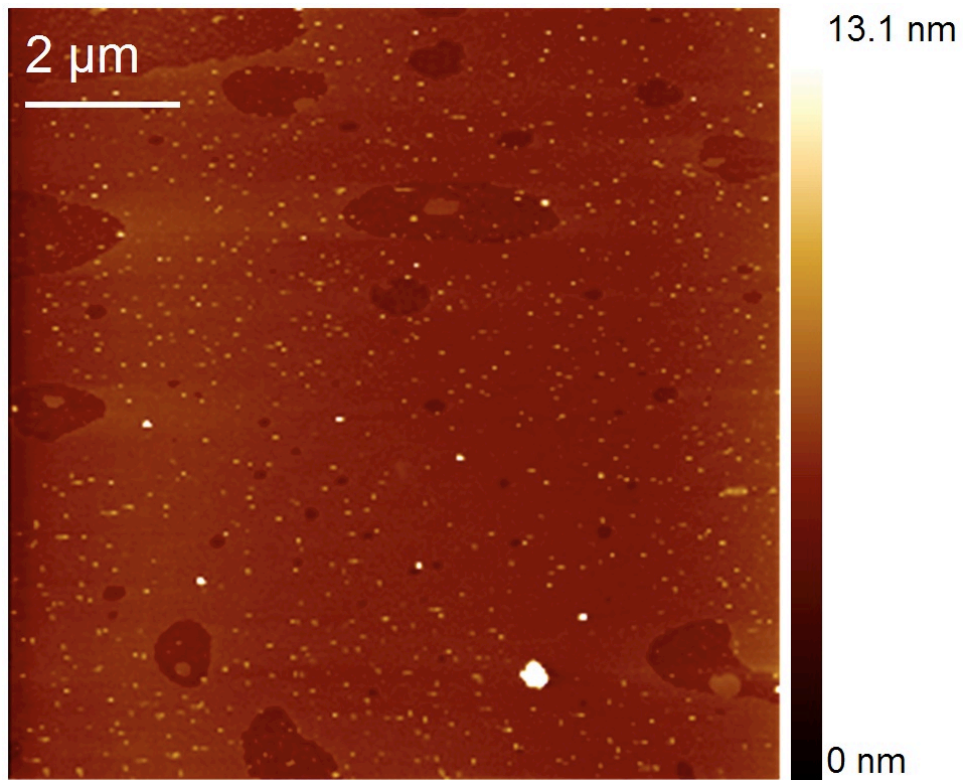**Figure 7:** Contact-mode AFM Image of h-BN sheets

Figure 8: Contact-mode AFM Image of h-BN sheets

Figure 7 shows sheets of h-BN dispersed on a mica substrate. Apparent in this scan is the extremely small lateral size exhibited by all of the sheets present. Also present is a sinusoidal ripple effect in this scan. This is an image artifact that could come from an optical interference from the laser or some external noise in the feedback signal. Figure 8 depicts another area of the same sample, and exhibits largely the same behavior as the material in figure 7. In addition to the h-BN sheets in this scan, we also see some portions of the substrate that have a lower height than the rest of the substrate. These holes likely come from portions of the mica substrate that were broken off unevenly during the cleaving process before the solution was placed on the substrate.

Figures 7 and 8 show a greater and more consistent dispersion of sheets than the previous experiment and the vast majority of h-BN sheets are less than 5 nm in thickness, with many as low as 1 nm. This is a good result bordering on monolayer thickness; unfortunately the extended sonication broke apart the h-BN into sheets of extremely small lateral size, which are not ideal for current applications of BNNSs. Therefore, extended sonication showed a decrease in sheet height, but at the cost of sheet size. Future experiments can account for this with shorter sonication periods and perhaps a change in sonication intensity, as the tip sonicator is a very powerful instrument.

Hummers Reacted h-BN

Figures 1, 3, and 5 provide a good example of the majority of Hummers reacted h-BN material. They show a somewhat inconsistent distribution with many thick h-BN sheets of more than 20 nm still present. These results are not ideal and do not indicate a widely successful process for large-scale BNNS retrieval. However, some exciting results from the Hummers treated material are shown in figures 9, 11, and 12; these scans may represent BNNSs of impressive lateral size. Figure 10 shows the cross section of one of these large sheets.
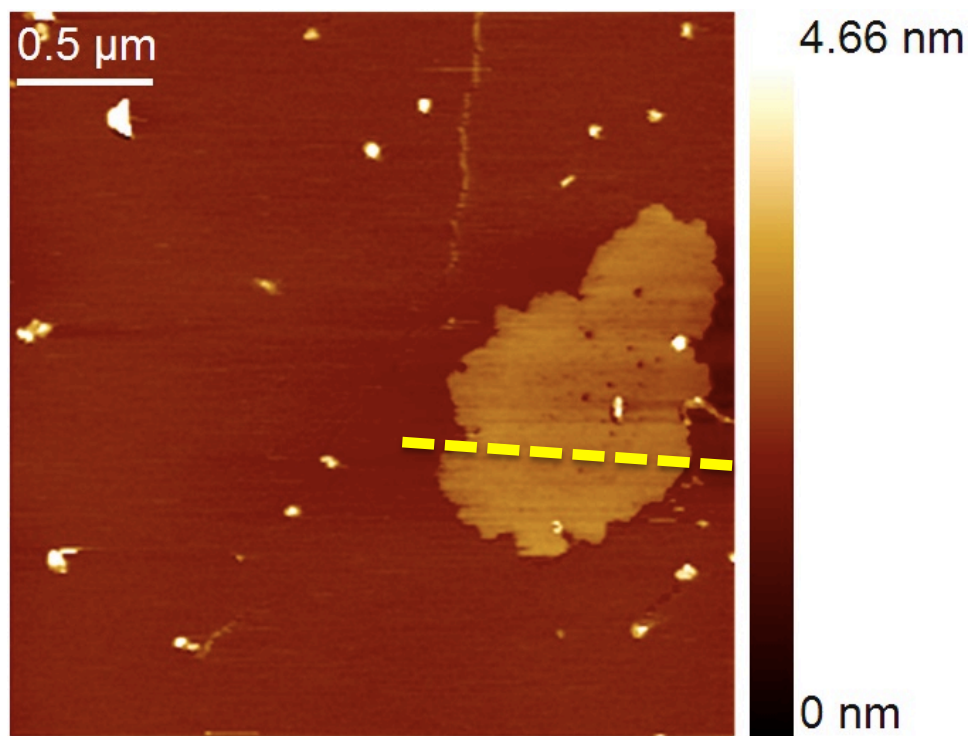
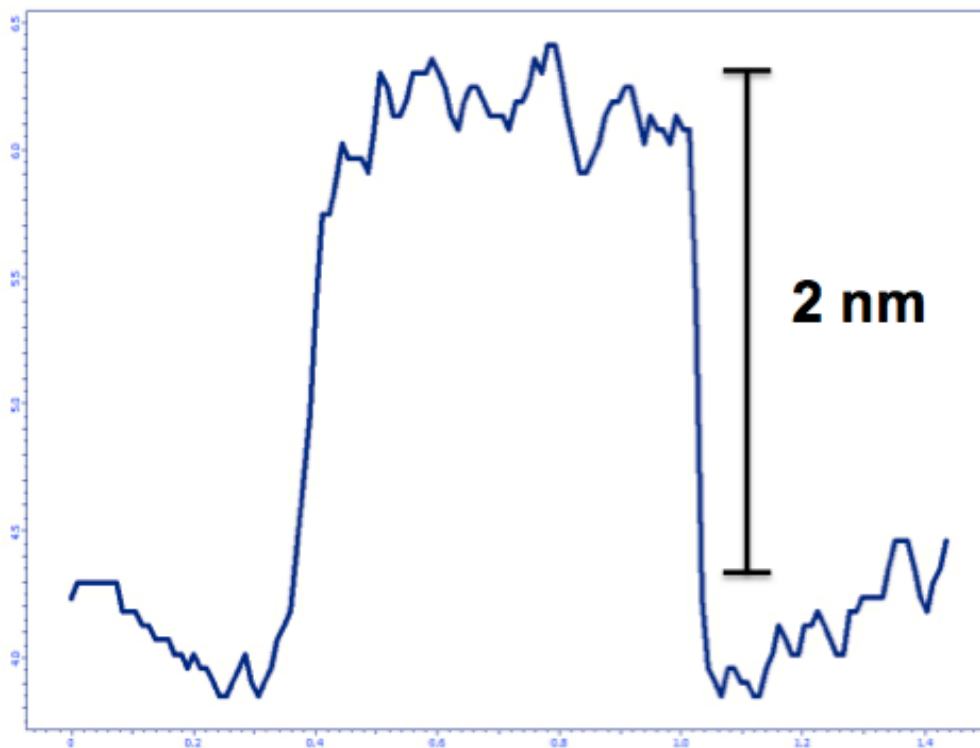**Figure 9:** Contact-mode AFM Image of large h-BN sheet from Hummers experiment

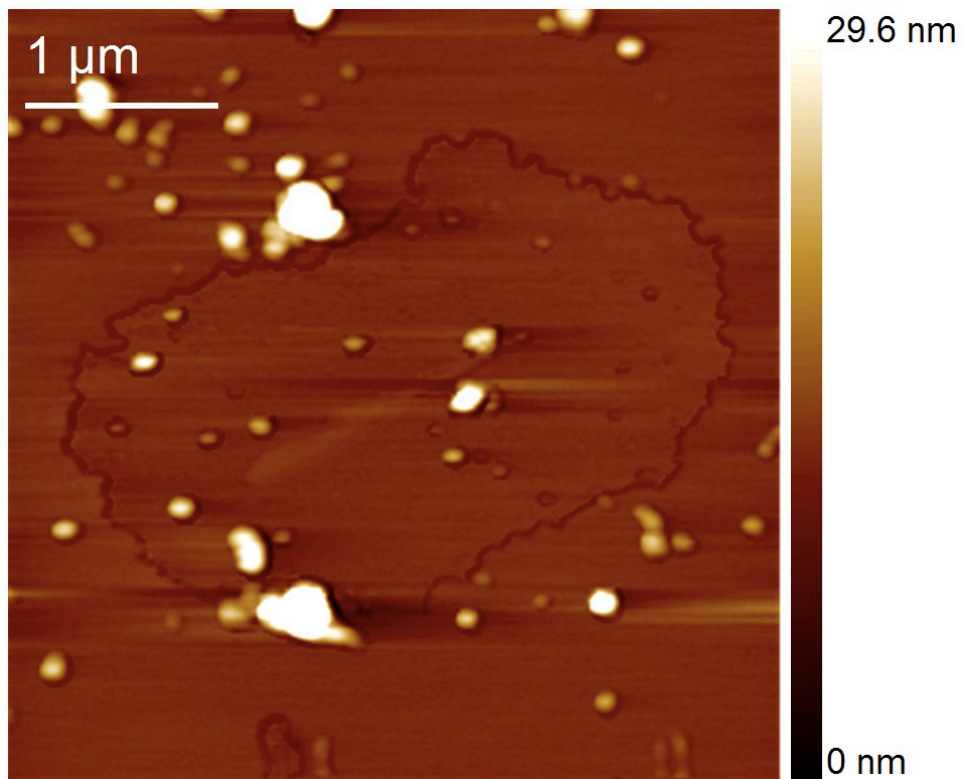**Figure 10:** Cross-section of thin h-BN sheet marked above

Figure 11: Semi-contact mode AFM Image of large h-BN sheet from Hummers experiment
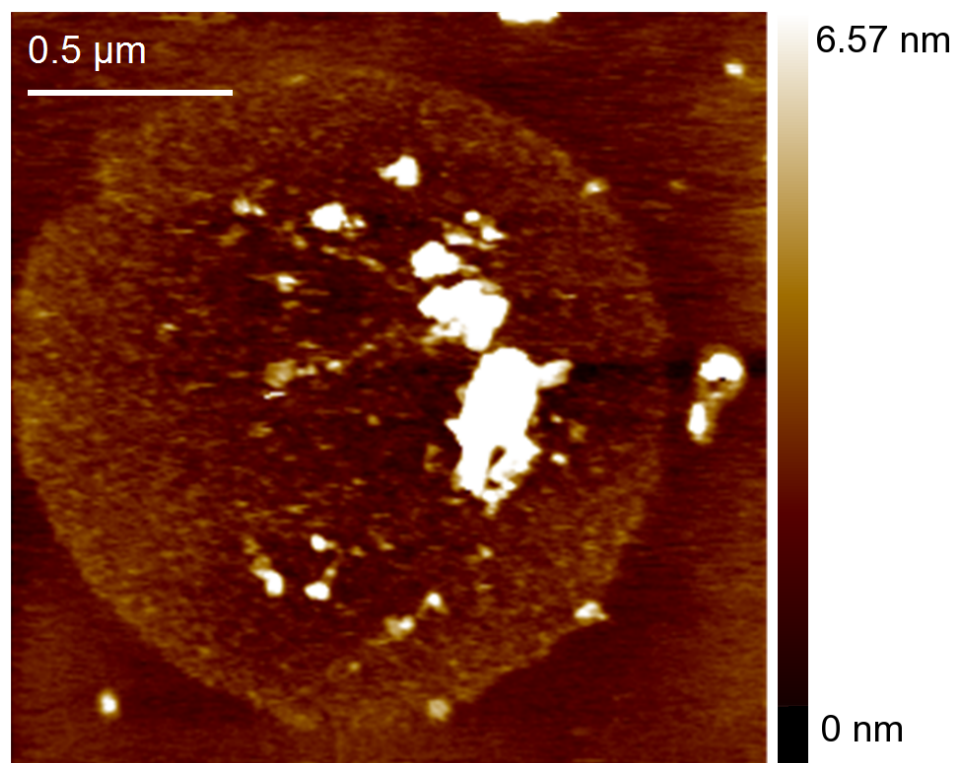

Figure 12: Contact-mode AFM Image of large h-BN sheet from Hummers experiment

Figure 9 shows an impressively sized sheet of h-BN surrounded by smaller and thicker sheets on a mica substrate. This particular sheet was discovered on the 4000 × g sample from the Hummers treated h-BN experiment. Figure 11 shows an even larger and thinner Boron Nitride sheet discovered in the 7000 × g sample from the Hummers experiment. This sheet was further investigated using phase signal analysis below. Figure 12 shows another notably large and thin sheet of h-BN. This sheet was perhaps the most peculiar one discovered in this experiment, as it is very circular in shape. This is suspicious and the sheet could actually be a droplet of contaminant liquid instead of Boron Nitride. This possibility was investigated and after repeated scanning of the sheet in contact mode the shape was still present and did not come apart as would likely happen if this were a droplet of contaminant. Therefore, we conclude that this is a circular sheet of h-BN that has been exfoliated to small thickness.

These sheets were found in low quantities in all three samples scanned in this experiment. With sheet heights of 1-3 nm and lateral sizes upwards of 1 µm, a large yield of these would be ideal for applications of BNNSs and an ideal result for this process. Figure 10 shows a sheet height of approximately 2 nm for the large sheet found in figure 9. This sheet is extremely thin while retaining a lateral size of over 1 µm. We hope to maximize the yield of these types of sheets with further experiments.

In order to study and validate the material these sheets consisted of, a further investigation into these especially large and thin sheets was made. Utilizing semi-contact mode AFM imaging, we studied the phase signal in hopes of confirming that these were indeed Boron Nitride sheets and not some other contaminant. Figures 13 and 14 show the results of this investigation.
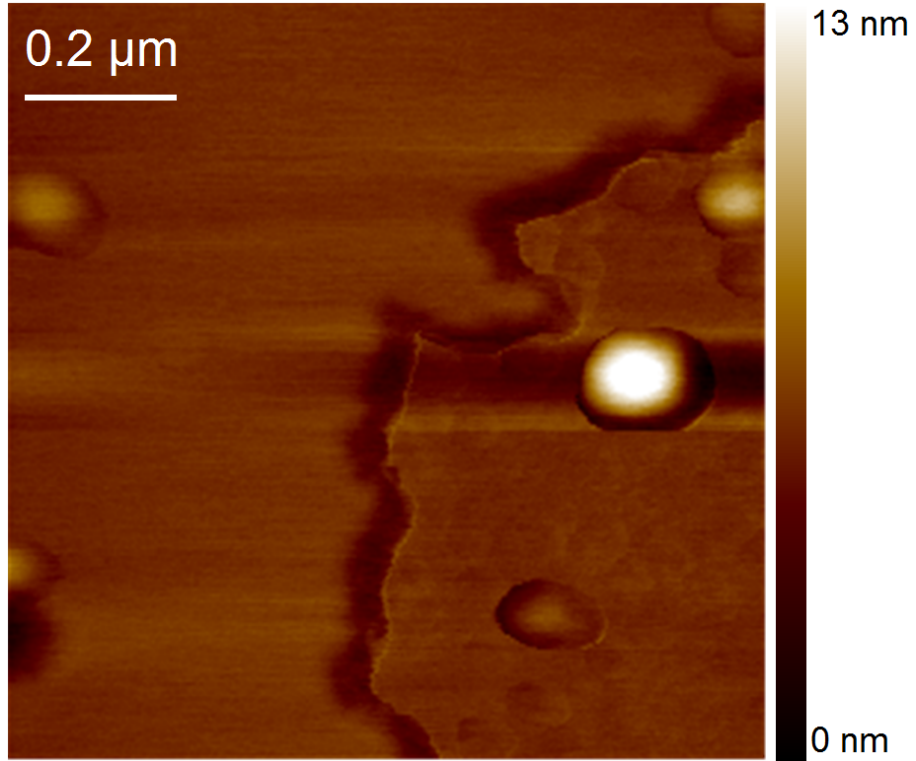
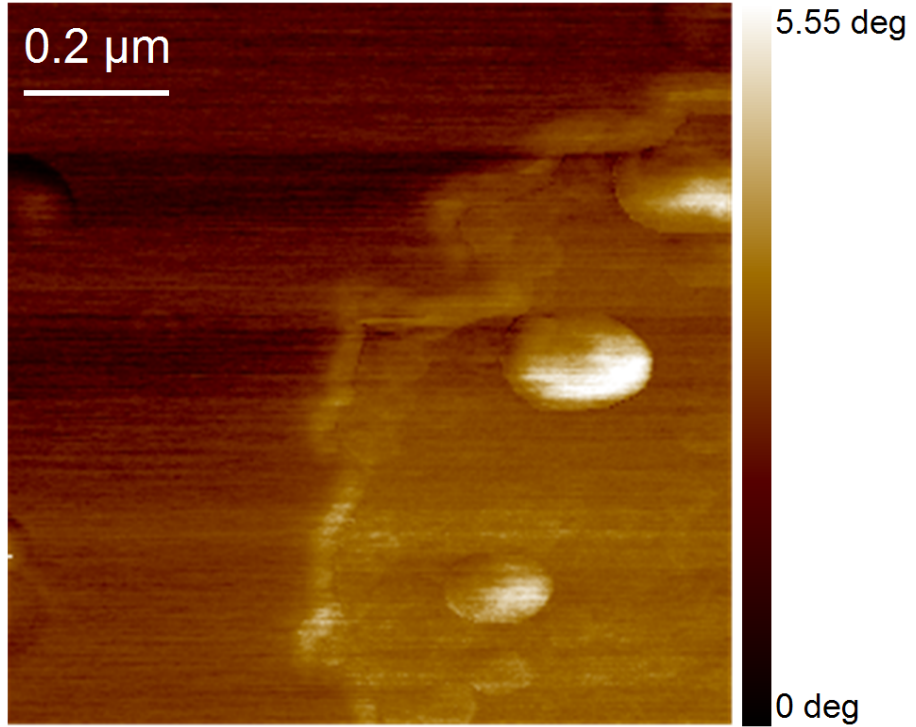**Figure 13**: Semi-contact mode AFM Image of large h-BN sheet, Height signal

Figure 14: Semi-contact mode AFM Image of large h-BN sheet, Phase signal

Figure 13 shows the height signal and figure 14 shows the phase signal of an up-close scan of the large sheet from figure 11. The phase signal shows a distinctly different phase value between the substrate and the material. This difference in phase value suggests that it is made up of a different material.[15] In addition, the phase of the large sheet matches with what we believe to be the thicker "chunks" of h-BN present on top of this sheet (these thick sheets are consistent with other thick h-BN sheets scanned in previous experiments). The phase data therefore provides evidence that these sheets are made of Boron Nitride and not some other material. Therefore we believe these scans represent minimal retrieval of BNNSs, which is a great step in the right direction.

Also seen in figure 13 is a large shadow outlining the border of the h-BN sheet. This outline makes it appear that the height of the substrate is much lower immediately after the sheet and then levels out further away from the sheet. This behavior is also visible around the larger sheets of Boron Nitride present on top of the thinner sheet. This is likely a scan artifact that comes from a bistability in semi-contact mode images that has been well studied in previous literature.[15]

Raw h-BN (No chemical treatment)

Here we repeated the centrifuge testing experiment with Raw h-BN that was not treated with the Hummers reaction. We hope to see conclusive evidence that the Hummers reaction makes exfoliation of h-BN significantly easier. Figures 15-22 show examples of discovered material during imaging of the three samples in the experiment.
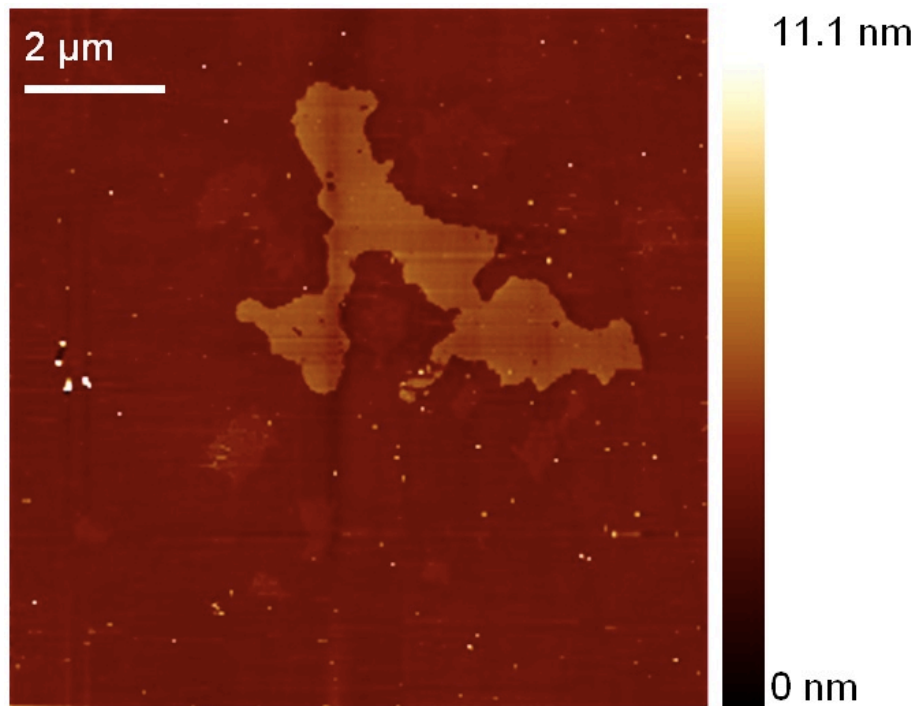
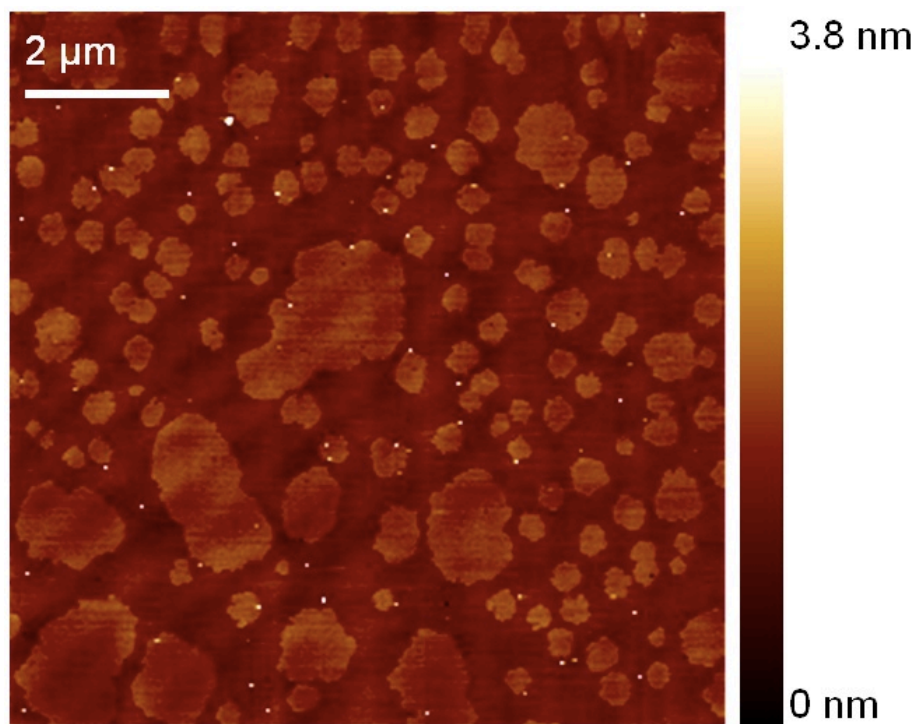**Figure 15:** Contact-mode AFM Image of large h-BN sheet from Raw, 4000 × g sample

Figure 16: Contact-mode AFM Image of h-BN sheets from Raw, 4000 × g sample
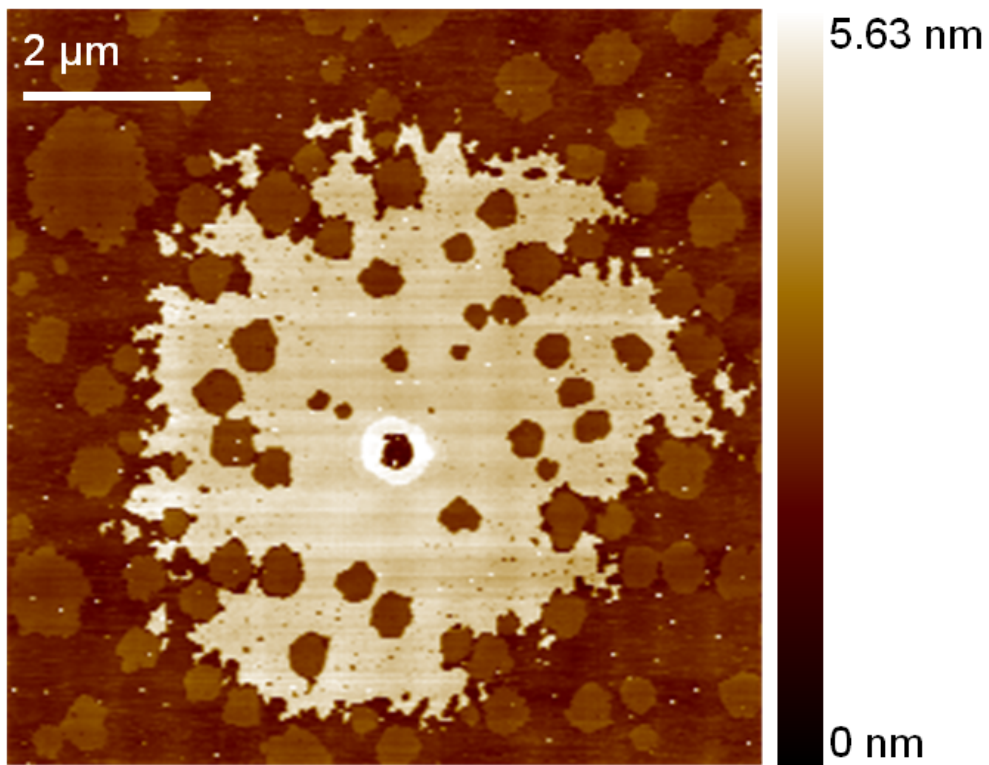
Figure 17: Contact-mode AFM Image of large h-BN sheet from Raw, 4000 × *g* sample

Figure 18: Contact-mode AFM Image of h-BN sheets from Raw, 7000 × *g* sample

Figure 19: Contact-mode AFM Image of h-BN sheet formation from Raw, 7000 × *g* sample
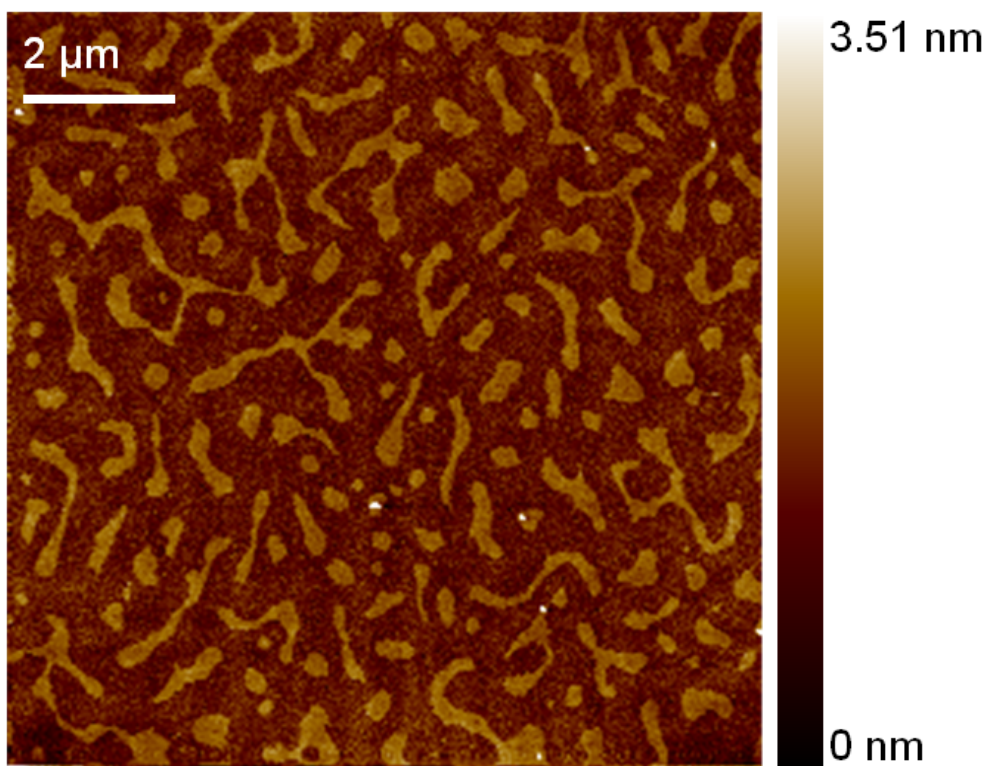

Figure 20: Close-up contact-mode AFM Image of h-BN sheet formation from Raw, 7000 × *g* sample

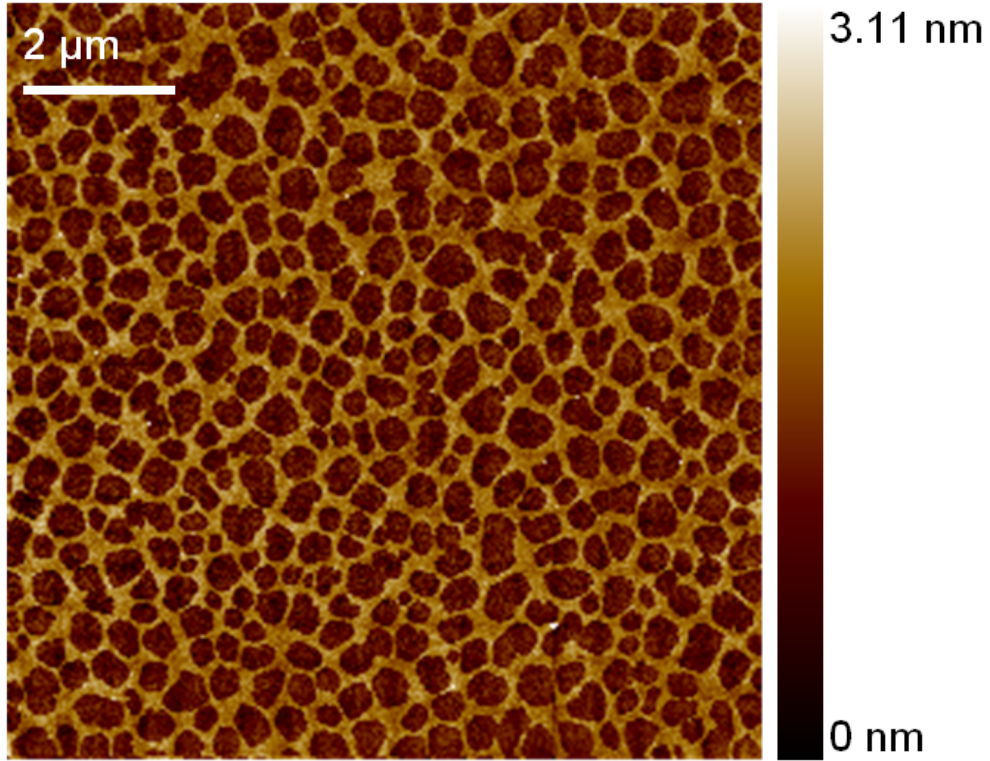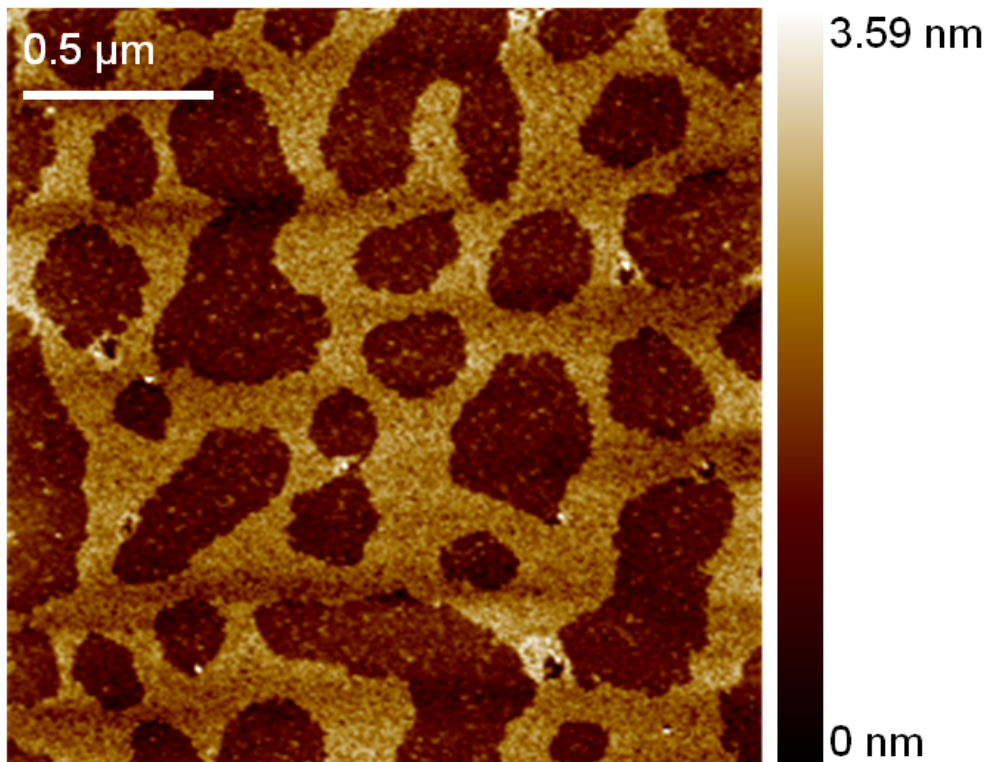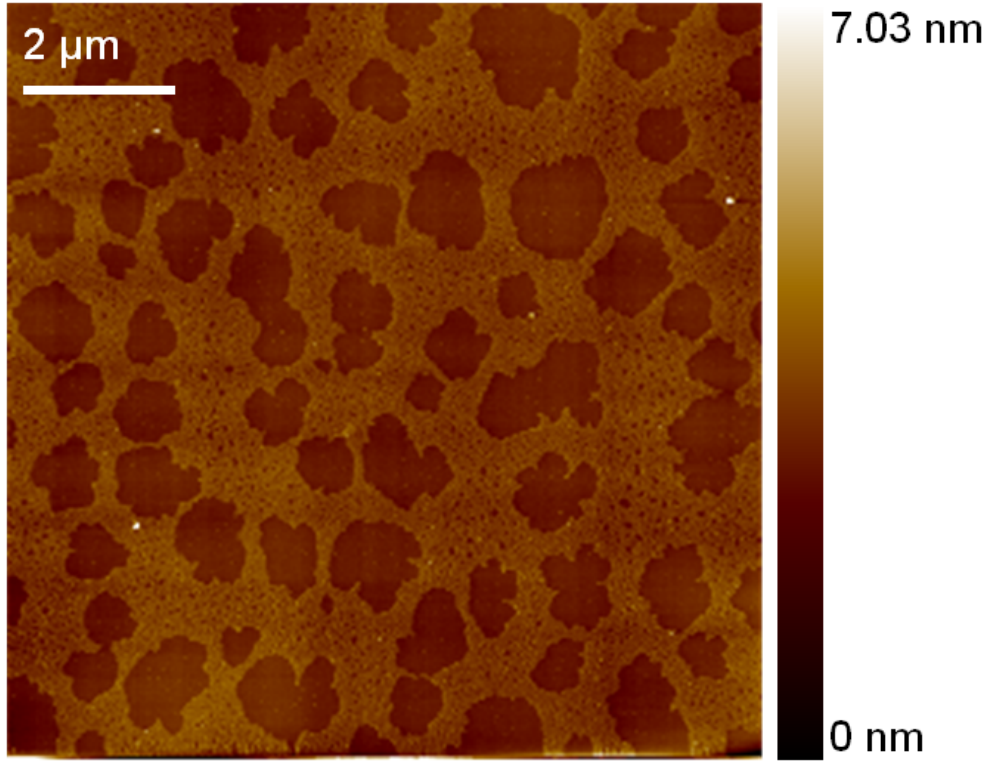**Figure 21:** Contact-mode AFM Image of h-BN sheet formation from Raw, 10 000 × *g* sample
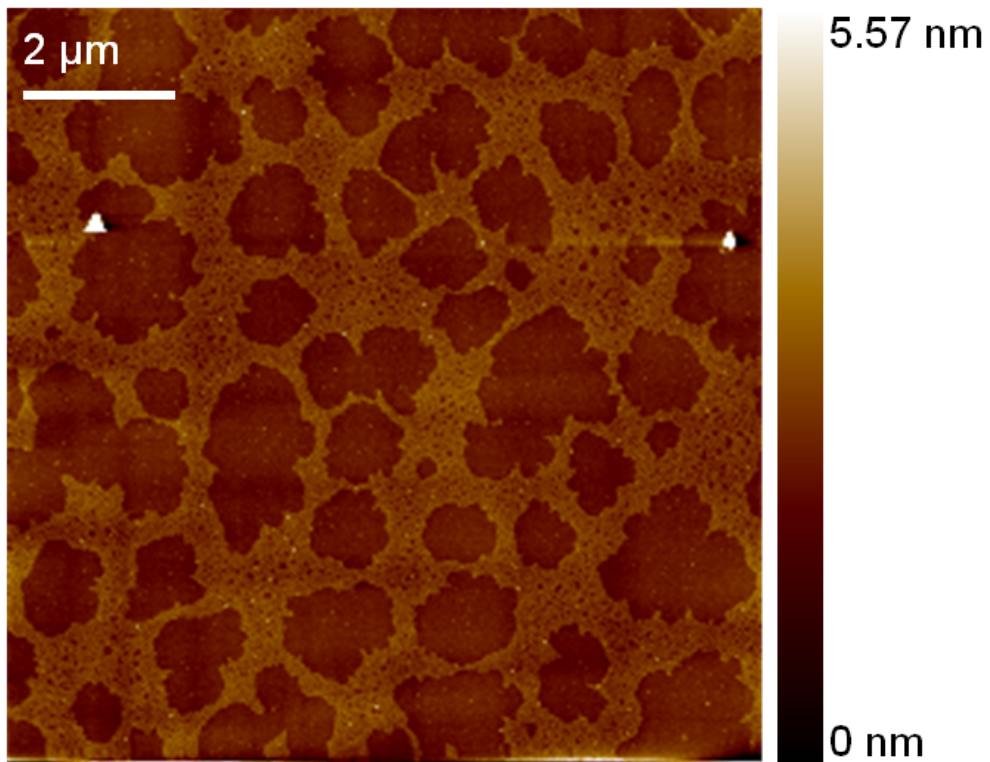

Figure 22: Contact-mode AFM Image of h-BN sheet formation from Raw, 10 000 × *g* sample

Apparent in these images is the presence of extremely large BNNSs appearing with more frequency than those from the Hummers h-BN experiment. These sheets have a thickness of a few nanometers and have much more intricate shapes than the BNNSs obtained in the previous experiment. The most peculiar result from these experiments is the bizarre formations present in some scans.

Figure 15 shows a large sheet similar to previous thin sheets in thickness but much larger in lateral size as it is almost 4 μm across on its longest axis. Figure 16 shows a very encouraging result with a high quantity of fairly large sized sheets with a thickness of less than 2 nm. A uniform distribution like this across an entire sample would be a strong indication of large scale BNNS exfoliation. Figures 17 and 18 show particularly bizarre formations of h-BN that could possibly be explained by the self-assembly of h-BN sheets during the spin coating process, while this is somewhat unlikely. Finally, figures 19-22 show the form of the majority of h-BN found in this experiment. Here, the material forms an interesting shape consisting of uniformly placed holes in the material of similar size and shape. Most intriguing is the small thickness of the material in these formations, with most of it being less than 3 nm. The strongest question that these results raise is how the material came together in this formation, especially on a large scale. This type of formation was not present any in previous experiments and is unique to the raw h-BN experiment. A possible explanation is that the concentration used (5 mg/mL) was high causing many sheets to settle in close proximity and assemble together into these arrangements. Either way, these are impressive results as they show a large amount of Boron Nitride material that has been separated to less than 3 nm in thickness, with many BNNSs present.

Another conclusion we can draw from scanning the raw h-BN sample is that there appears to be no major difference in BNNS retrieval between the Hummers reacted and non-reacted Boron Nitride. We see similar sheets of small (< 3 nm) thickness in both trials with perhaps more in the raw experiment. This result most likely stems from the chemical stability of Boron Nitride mentioned before that hinders the effectiveness of the Hummers treatment.

Solvent Variation

This experiment was completed to test two different solvents (DMF and IPA) to see if either solvent makes a greater impact on the effectiveness of the exfoliation process. Figures 23 and 24 show some sample scans from the DMF trial. Figures 25 and 26 show resultant scans from the IPA trial.
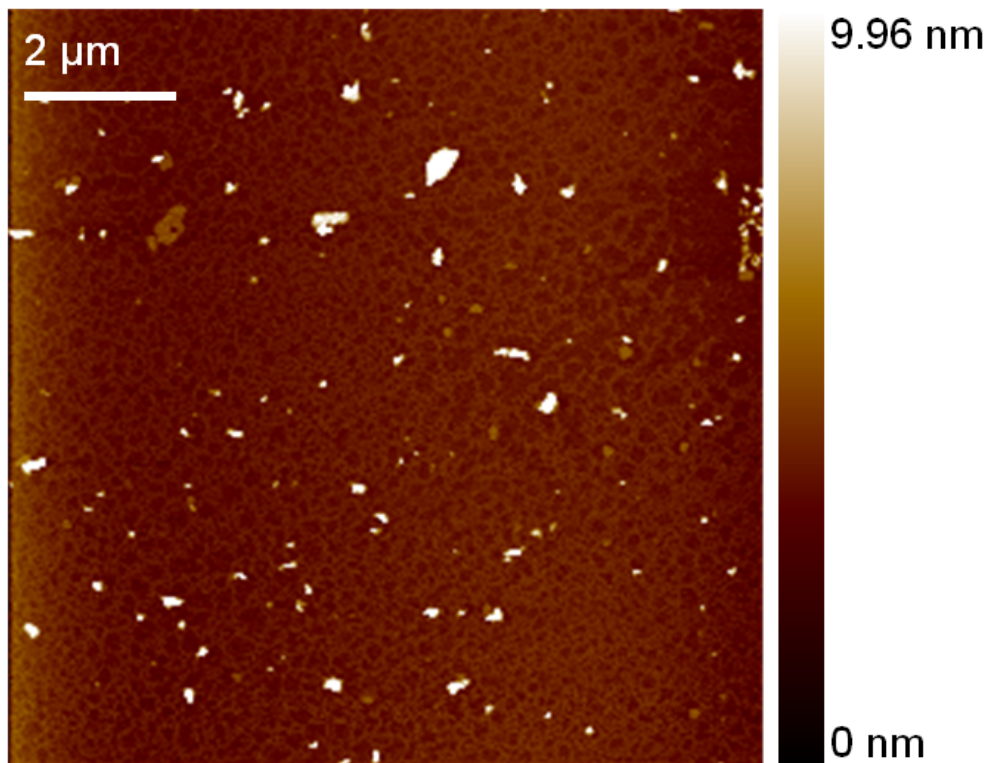

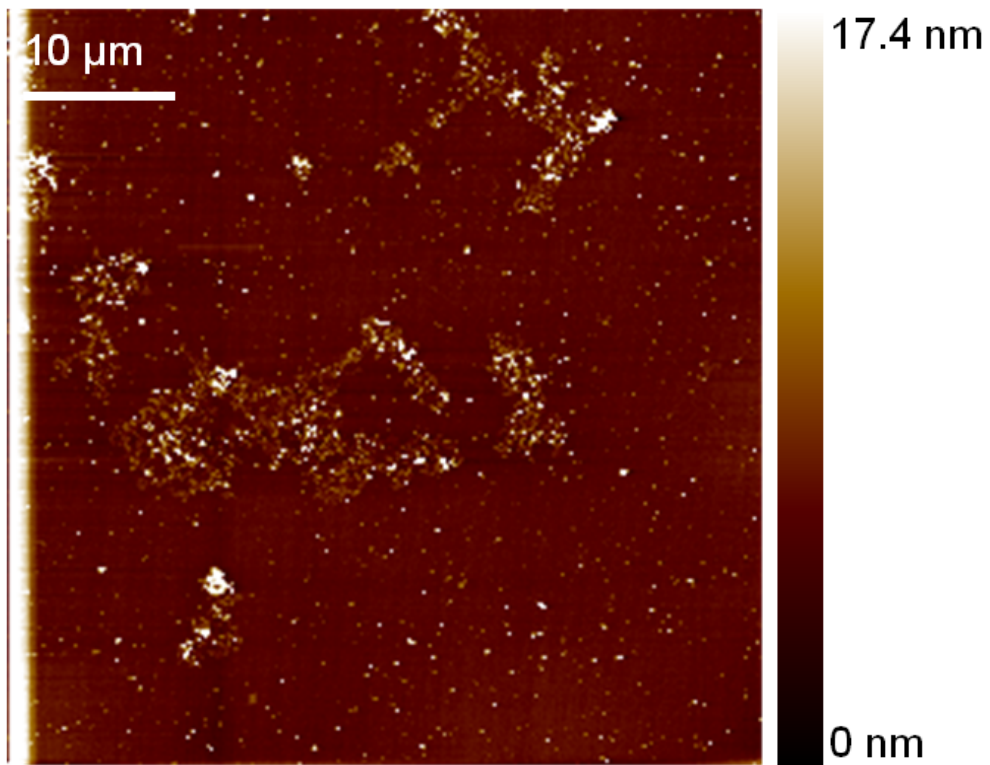**Figure 23:** Contact-mode AFM Image of h-BN sheets from DMF sample

Figure 24: Contact-mode AFM Image of h-BN sheets from DMF sample
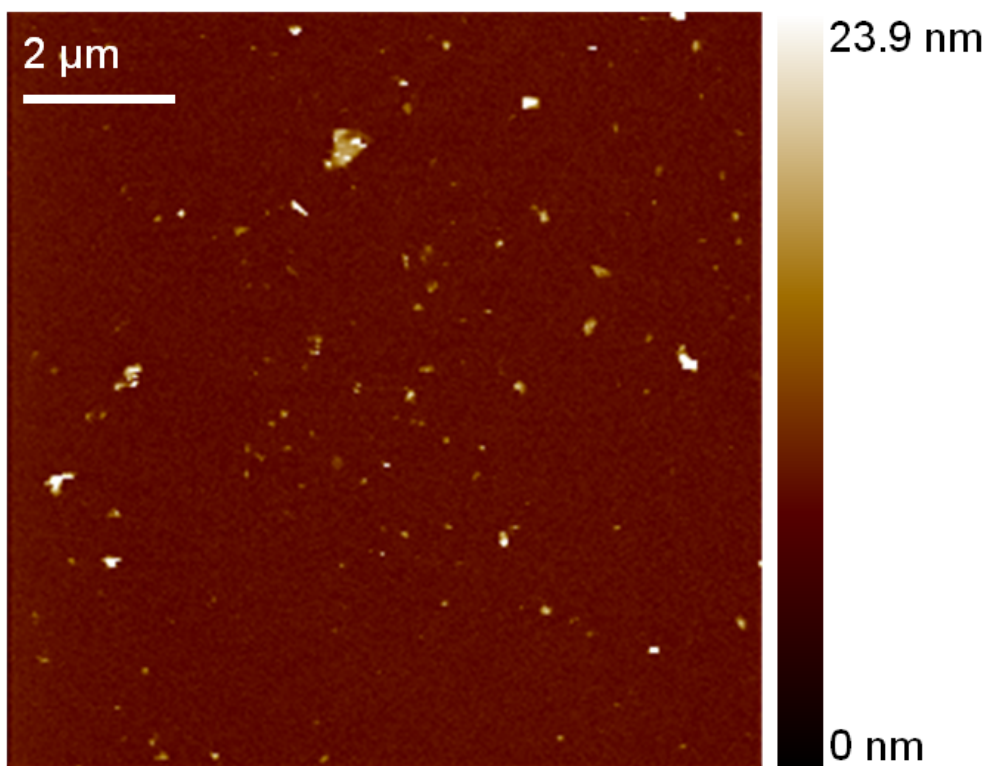

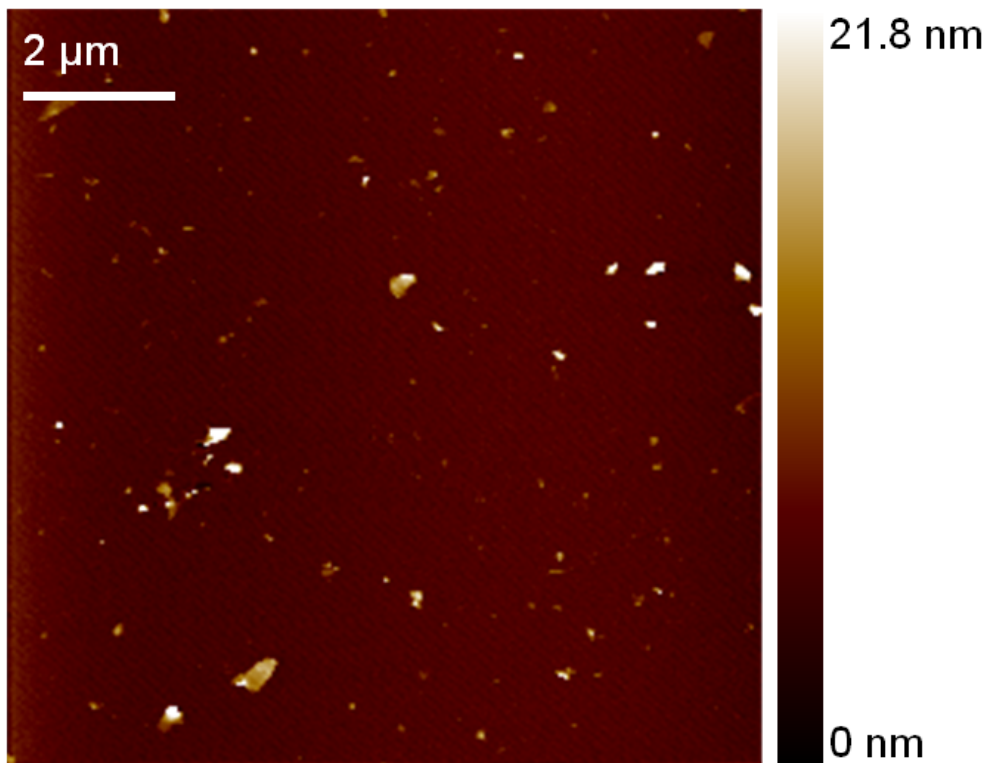**Figure 25:** Contact-mode AFM Image of h-BN sheets from IPA sample

Figure 26: Contact-mode AFM Image of h-BN sheets from IPA sample

Figure 23 shows a large collection of h-BN sheets on a mica substrate with a thickness of about

20 nm. While a few of these sheets exhibit promising lateral size of around 1 μm, most of the

material in this scan has insignificant lateral size. Figure 24 gives a larger scan size and shows a

number of h-BN sheets gathered in higher density. Also present in figure 24 are possible

formations of material that likely consists of small h-BN sheets that have possibly come together

as a result of the centrifugal force from the spin coating process. Formations of these shapes

were found somewhat consistently in this DMF experiment and could be an exciting breakthrough

considering their relatively small thickness (< 3 nm at some points) and large lateral size.

Figures 25 and 26 show h-BN material on a mica substrate after sonication in IPA instead

of DMF. Here, sheets of Boron Nitride are in roughly the same distribution as the material

obtained from sonication in DMF. Similar to the DMF sample, scans from the IPA experiment

consist of mostly small h-BN sheets with a few thicker sheets of larger lateral size dispersed

sparingly. Not present in the IPA scans were the h-BN formations that appeared prevalently in the DMF experiments.

While it's hard to conclude that this behavior of sheet formation and possible assembly is unique to DMF, especially since IPA was not as thoroughly examined as DMF in this research, it appears that these formations of h-BN do not occur in IPA. Otherwise, the results show no significant difference in the quality of exfoliated Boron Nitride material. Therefore, without extensive qualitative analysis, we can make a hesitant conclusion that DMF is a more ideal solvent than IPA, although there does not seem to be a significant increase in the success of the exfoliation process during sonication for either solvent. Instead, DMF seems to be a better solvent due to the interesting behavior h-BN material after sonication and centrifugation possibly due to the spin coating process.

Conclusion

The results from this project show some significant progress toward the goal. In our first experiment we were able to show that the combination of sonication and centrifugation shows effectiveness in separating h-BN to several nanometer thickness and we even retrieved BNNSs in small quantities. Centrifugation was seen to be a valuable aspect to the process as previous experiments that did not utilize centrifugation yielded some h-BN sheets that were extremely thick and difficult to scan with AFM.[16] We could not make a concrete conclusion as to the relationship between RCF value during centrifugation and the thickness of exfoliated material obtained. This lack of conclusion was due to uncertainty in the method for characterizing average sheet thickness in each experiment and the fact that there was no significant difference in the yield of the different centrifuge speeds tested.

We were able to engineer a successful method for gathering lateral size data of exfoliated material, which is important for comparing different methods of exfoliation. Unfortunately, we were unsuccessful in establishing a similar method for gathering data on sheet height. Still, using atomic force microscopy we were able to compare different methods of exfoliation and different parameters in the process to see what results in the most desirable material retrieved.

We also studied the effect of the Hummers reaction on exfoliation of Boron Nitride in hopes that it would yield similar results to its treatment of graphite. Through our investigation we gathered that there was no major noticeable difference between the quality of exfoliated material obtained after treatment with the Hummers reaction. This is an unfortunate result that likely stems from the strong chemical stability of Boron Nitride, an attribute not present in graphite, that makes the effect of the Hummers treatment less pronounced and insignificant with regards to exfoliation.

Additionally, we introduced multiple solvents into the sonication process to see if one was more effective in separating h-BN. We showed that DMF appeared to be a more ideal solvent for this process, although it did not seem to make a noteworthy difference in the thickness and size of h-BN material exfoliated.

Encouraging in this experiment was the exciting number of BNNSs found during scanning. We believe that the presence of large-sized h-BN sheets of less than 3 nm in thickness is a significant result that suggests this exfoliation method is a good candidate for further investigation. Unfortunately, it is still a far cry from a functional large-scale exfoliation method.

Overall, the results from this project are promising and fruitful. We have successfully exfoliated h-BN to several nanometers in thickness and have generated small quantities of large sized BNNSs. Still, much of the exfoliated h-BN retained undesirable thickness and size so there is room for improvement before this process is declared efficient and successful on a large scale. We have shown that combining sonication and centrifugation can be greatly beneficial in exfoliating Boron Nitride. This represents a significant step in the direction of an ideal exfoliation process that produces high quantities of BNNSs with significant lateral size.

Acknowledgements

       I would like to thank Laura Rickard, Minzhen Cai, and Arthur Jaeton Glover for their support and advice during my research. I would especially like to thank Daniel Thorpe for helping me start this project and for treating the Boron Nitride with the Hummers method. Lastly, I would like to thank Dr. Hannes Schniepp for his knowledge and guidance during this process.

References

1. Golberg, D., Y. Bando, Y. Huang, T. Terao, M. Mitome, C. Tang, and C. Zhi. 2010. "Boron Nitride Nanotubes and Nanosheets." *Acs Nano* 4 (6): 2979-2993.

2. Lin, Y., T. V. Williams, and J. W. Connell. 2009. "Soluble, Exfoliated Hexagonal Boron Nitride Nanosheets." *The Journal of Physical Chemistry Letters* 1 (1): 277-283.

3. Zhi, C., Y. Bando, C. Tang, H. Kuwahara, and D. Golberg. 2009. "Large‐Scale Fabrication of Boron Nitride Nanosheets and their Utilization in Polymeric Composites with Improved Thermal and Mechanical Properties." *Advanced Materials* 21 (28): 2889-2893.

4. Haubner, R., M. Wilhelm, R. Weissenbacher, and B. Lux. 2002. "Boron nitrides—properties, Synthesis and Applications." *High Performance Non-Oxide Ceramics II*: 1-45.

5. Engler, M., C. Lesniak, R. Damasch, B. Ruisinger, and J. Eichler. 2007. "Hexagonal Boron Nitride (hBN): Applications from Metallurgy to Cosmetics." *Ceramic Forum International* 84: E49-E53.

6. Harrison, C., S. Weaver, C. Bertelsen, E. Burgett, N. Hertel, and E. Grulke. 2008. "Polyethylene/boron Nitride Composites for Space Radiation Shielding." *Journal of Applied Polymer Science* 109 (4): 2529-2538.

7. Warner, J. H., M. H. Rümmeli, A. Bachmatiuk, and B. Büchner. 2010. "Atomic Resolution Imaging and Topography of Boron Nitride Sheets Produced by Chemical Exfoliation." *ACS Nano* 4 (3): 1299-1304.

8. Widenkvist, E., DW Boukhvalov, S. Rubino, S. Akhtar, J. Lu, RA Quinlan, MI Katsnelson, K. Leifer, H. Grennberg, and U. Jansson. 2009. "Mild Sonochemical Exfoliation of Bromine-Intercalated Graphite: A New Route Towards Graphene." *Journal of Physics D: Applied Physics* 42: 112003.

9. Lin, Y., T. V. Williams, T. B. Xu, W. Cao, H. E. Elsayed-Ali, and J. W. Connell. "Aqueous Dispersions of Few-Layered and Monolayered Hexagonal Boron Nitride Nanosheets from

Sonication-Assisted Hydrolysis: Critical Role of Water." *The Journal of Physical Chemistry C*.

10. Hummers Jr, W. S. and R. E. Offeman. 1958. "Preparation of Graphitic Oxide." *Journal of the American Chemical Society* 80 (6): 1339-1339.

11. Schniepp, H. C., J. L. Li, M. J. McAllister, H. Sai, M. Herrera-Alonso, D. H. Adamson, R. K. Prud'homme, R. Car, D. A. Saville, and I. A. Aksay. 2006. "Functionalized Single Graphene Sheets Derived from Splitting Graphite Oxide." The Journal of Physical Chemistry B 110 (17): 8535-8539.

12. Coleman, J. N., M. Lotya, A. O'Neill, S. D. Bergin, P. J. King, U. Khan, K. Young, A. Gaucher, S. De, and R. J. Smith. 2011. "Two-Dimensional Nanosheets Produced by Liquid Exfoliation of Layered Materials."*Science* 331 (6017): 568.

13. Lin, Y., T. V. Williams, W. Cao, H. E. Elsayed-Ali, and J. W. Connell. "Defect Functionalization of Hexagonal Boron Nitride Nanosheets." *The Journal of Physical Chemistry C*.

14. Erickson, K. J., A. L. Gibb, A. Sinitskii, M. Rousseas, N. Alem, J. M. Tour, and A. K. Zettl. "Longitudinal Splitting of Boron Nitride Nanotubes for the Facile Synthesis of High Quality Boron Nitride Nanoribbons." *Nano Letters*.

15. García, R. and R. Perez. 2002. "Dynamic Atomic Force Microscopy Methods." *Surface Science Reports* 47 (6): 197-301.

16. Thorpe, Daniel and Schniepp, H. C. 2011. Unpublished data.