

# Synthesis, characterization, and purification of boron nitride nanotubes intercalated with magnesium

Roxana J. Moraga, Gabriela Fuentes, Tu Nguyen, Zubeda Vaid, Narayan S. Hosmane.

NORTHERN ILLINOIS UNIVERSITY, Department of Chemistry and Biochemistry. 1425 W Lincoln Highway, DeKalb, IL.

**KEYWORDS:** Boron Nitride Nanotubes, Carbon Nanotubes, intercalation, magnesium, nanotubes, lithium.

---

**ABSTRACT:** Intercalation of Boron Nitride Nanotubes (BNNTs) with magnesium (Mg) is explored due to its potential super-conductive properties. Various syntheses were performed under different sets of conditions in order to optimize reaction conditions. These include the presence of zinc as a catalyst and the temperature at which the reaction is carried out (either 700 or 800°C). All products were then analyzed and characterized, using methods such as Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Energy-dispersive X-ray Spectroscopy (EDX), and Fourier-Transform Infrared Spectroscopy (FTIR). Both TEM and FTIR results confirmed the formation of BNNTs, and EDX showed the presence of magnesium in the product, indicating possible intercalation with Mg. A purification method for the crude product was established, and the purified product was further characterized. Results indicated the tubes became clearer after purification, however, some impurities remain. Purification methods must be further investigated.

---

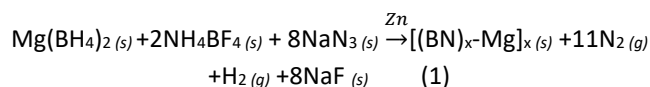
**INTRODUCTION.** Boron Nitride Nanotubes, or BNNTs, have been the subject of extensive research in recent years, due to their various properties (Ciofani, 2013). Some of these include high hydrophobicity, resistance to oxidation, and they are noncytotoxic, making them excellent as biological nanocarriers (Zhi, 2008). BNNTs also exhibit piezoelectricity, or the ability to conduct electricity under pressure or stress. These properties have allowed applications of BNNTs to be explored in various fields such as medicine (Ricotti, 2013), physics, and electronics (Feng, 2014).

Despite these beneficial properties, BNNTs poor conductivity is a disadvantage for those exploring applications in the development of electronic devices, sensors, etc. In recent years, the doping of Carbon Nanotubes (CNTs), analogs of BNNTs, with lithium have been found to increase the reaction energies, and expand both covalent and non-covalent chemistry of these structures (Denis, 2011). Because CNTs and BNNTs share so many characteristics, researchers believe the same kind of encapsulation or intercalation of metals can expand the electrical conductivity properties of BNNTs (Feng, 2014). In fact, intercalating BNNTs with various metals or other materials has been seen to significantly modify their electronic or magnetic properties (Golberg, 2001). Therefore, it has now become of interest to explore what the effects of metal intercalation are for BNNTs and what potential applications they can be used for.

## MATERIALS AND PROCEDURE.

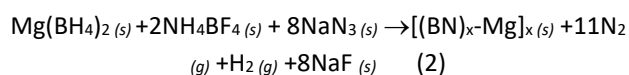
**Synthesis:** Mg(BH<sub>4</sub>)<sub>2</sub> was obtained from Sigma-Aldrich (St. Louis, MO). All other reactants (NH<sub>4</sub>BF<sub>4</sub>, NaN<sub>3</sub>, and Zn) were available from lab.

Two types of reactions were performed, first using Zn as a catalyst and later without Zn. The following reaction scheme for the synthesis of Mg-intercalated BNNT with Zn as a catalyst was used:



All reagents and pertinent equipment were transferred into the glove box, after appropriate vacuuming and purging with Argon. The reactants were then weighed, grinded, and transferred into a pressure vessel, and later sealed. The pressure vessel was then placed into a furnace for a pyrolysis reaction using the temperature program outlined in Table 1.

The following reaction scheme for the synthesis of Mg-intercalated BNNT without Zn as a catalyst was used:



All procedures were followed as in the previous reaction. Temperature conditions were also varied, with some reactions performed at 700°C and others at 800°C.

Table 1. Temperature program followed for pyrolysis reaction. Total running time is 18 hours and 21 minutes.

Step	Program	Value	Step	Program	Value	Step	Program	Value
1	C01	0°C	7	C04	600°C	13	C07	700°C
2	T01	40 min	8	T04	20 min	14	T07	120 min
3	C02	200°C	9	C05	600°C	15	C08	200°C
4	T02	20 min	10	T05	20 min	16	T08	-121
5	C03	200°C	11	C06	700°C			
6	T03	40 min	12	T06	720 min			

**Purification:** Approximately 1g of crude product was ground and placed into a 400mL beaker. Around 150-200mL of 95% ethanol were added to the beaker. Using a probe-type sonicator, the mixture was sonicated for 1 hour. After sonication, the mix was allowed to settle for about 10 minutes. Using a pipette, the supernatant was transferred to a 500mL round bottom flask. The flask was then placed into a Rotovap, where the product was completely dried. This was stored overnight.

Later, a mixture of 100 mL DI water and 150 mL HCl was prepared and poured into the flask containing the dried product. The diluted acid solution and product were once again sonicated for 1 hour. Once this process ended, the product was vacuum filtered. The residue left over was dried and transferred to a small vial for characterization.

**RESULTS AND DISCUSSION.** The first synthesis using zinc as a catalyst proceeded at 700°C and produced a mostly white product, with some gray particles scattered between, as can be seen in Figure 1. The gray coloring was assumed to be due to zinc dust.

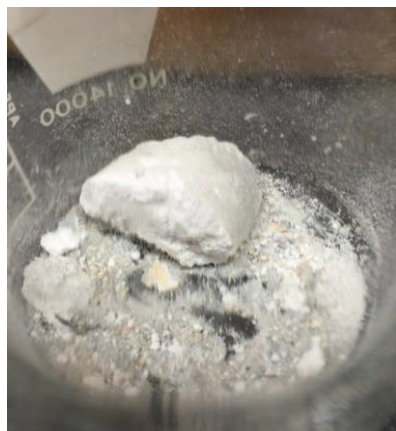


Figure 1. Raw product obtained in first reaction using zinc as the catalyst.

A sample of the product was analyzed using transmission electron microscopy (TEM), however none of the images obtained showed any indication of the formation of tubes (Figure 2). It was assumed this occurred due to the zinc, which may

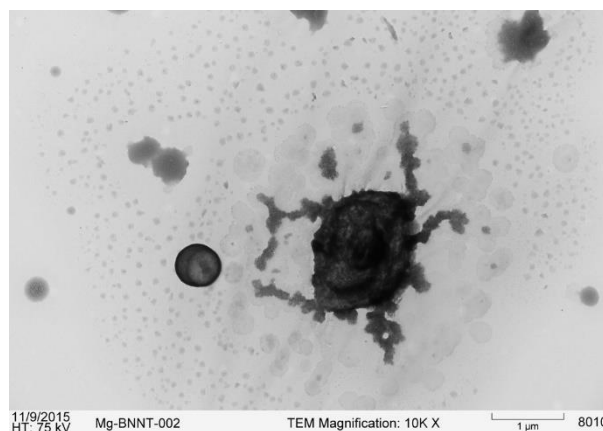


Figure 3. Raw product obtained in second reaction in the absence of zinc.

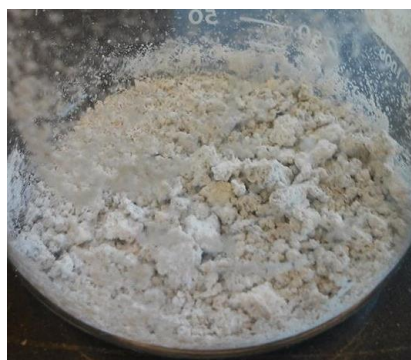


Figure 2. TEM results for synthesis of Mg-intercalated BNNT using Zn as the catalyst.

have caused on over-reaction due to its catalytic properties. For this reason, it was decided to remove zinc from the reaction.

The next reaction was performed without zinc as the catalyst, also

running at a temperature of 700°C. This time the product was observably different in texture, appearing lighter and more porous, and in color, as it was much whiter (Figure 3).

A sample of this product was also analyzed using TEM. Large amounts of tubes were visible, differing in shape and size. The tubes appeared to be rough in texture, with spikes protruding from their surface. These spikes were believed to possibly be the result of the metal Mg intercalated within the surface of the BNNT. Other rounded

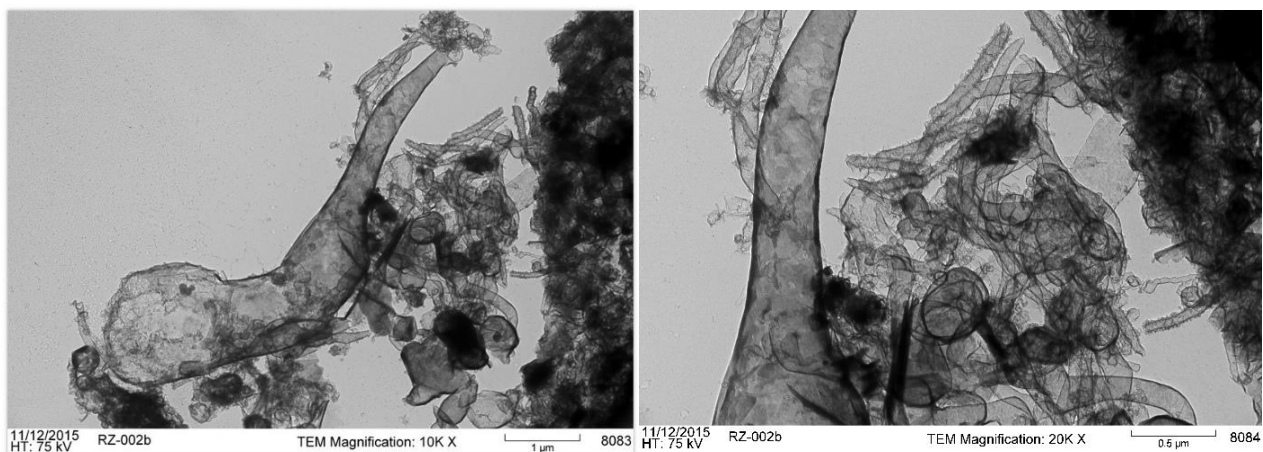


Figure 4. TEM of product obtained without using zinc as a catalyst. The formation of tubes differing in size and shape can be seen. The texture is not consistent throughout, as some tubes appear to be smooth while others are more jagged. Some rounded structures (nanocages) can be observed on the right.

structures were also observed in the sample, which appeared to be nanocages (Figure 4). To confirm the formation of BNNTs, the sample was taken for FTIR analysis. The spectra we obtained showed characteristic BNNT peaks: B-N-B at around 800 and B-N at 1300, as well as an OH peak which can be seen at approximately 3500 (Figure 5). Although the TEM and FTIR results for the presence of BNNTs were very promising, an additional reaction was performed in order to see if cleaner tubes could be produced.

Another synthesis reaction was performed, once more without using the catalyst zinc. The temperature for this reaction was changed from 700°C to 800°C. It was observed that the higher temperature caused some of the equipment to melt (specifically, the gasket) and contaminate the product. Because of this, the decision was made to maintain the pyrolysis temperature set at 700°C for all future reactions.

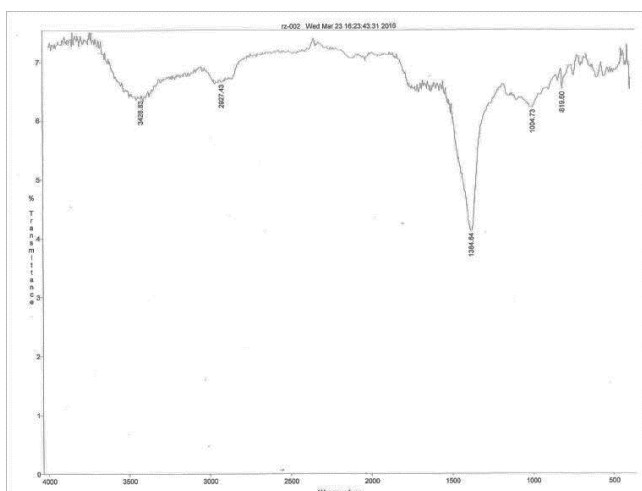


Figure 5. FTIR data for RZ-002, first reaction performed in the absence of Zn and at 700°C.

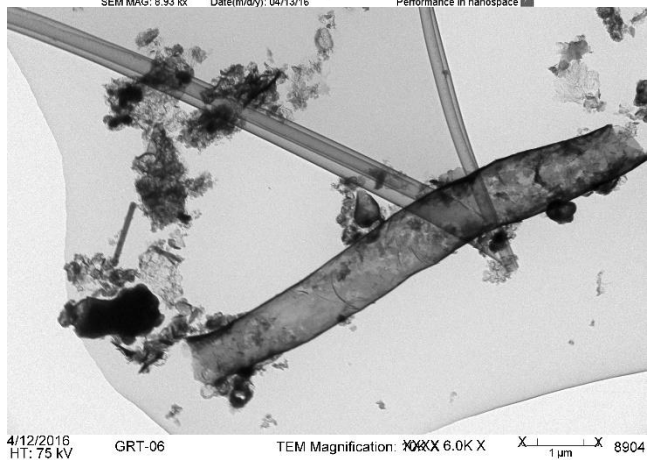
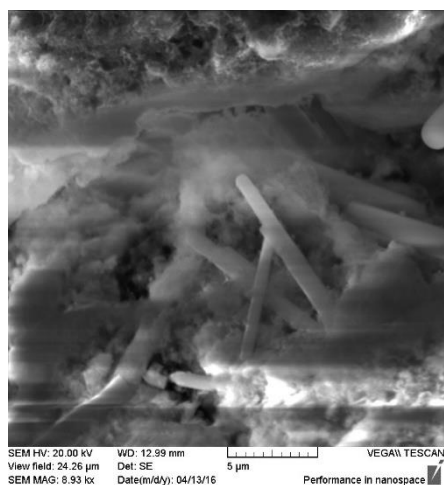


Figure 6. GRT06, second synthesis performed in the absence of Zn and at 700°C. Above, SEM shows the tubes formed and gathered into clusters. Below, TEM of the product shows the formation of tubes differing in size.

The second reaction described here was replicated (same reaction and temperature) as it produced the best quality product. Furthermore, other forms of product analysis were used for this reaction, including SEM and EDX. The raw

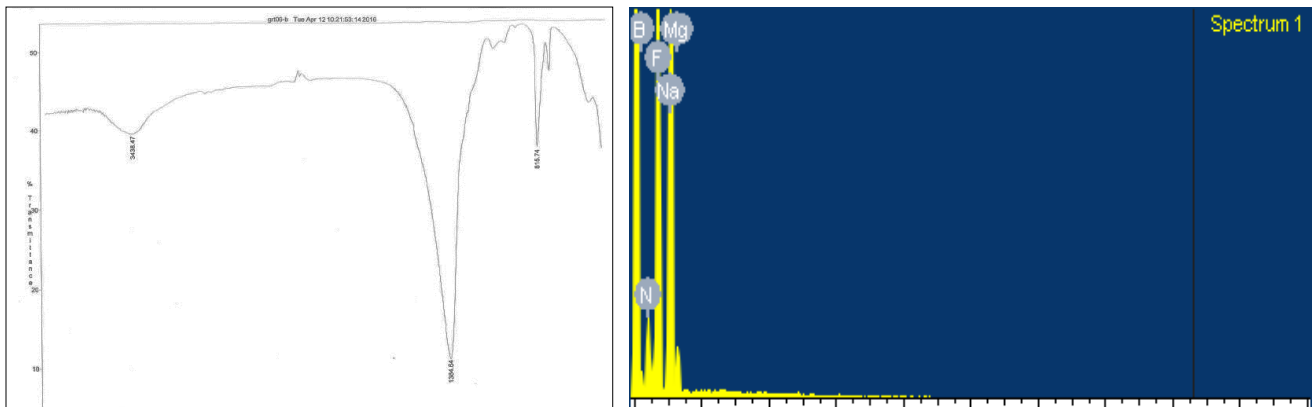


Figure 7. FTIR and EDX of GRT06. On the left, FTIR shows characteristic BNNT peaks, B-N-B and B-N at \_\_\_ and \_\_\_, respectively. On the right, EDX results show that Mg is present in the product.

product was similar in appearance to the previous reaction. TEM analysis showed once again the formation of tubes differing in size. Additionally, other structures could be seen which were much thinner and longer—these were thought to be nanorods. Hair-like structures on the surface of the tubes were also observed. These are important because the literature states these structures are indicative of intercalation having occurred. SEM analysis showed clean images of the surface of these tubes (and/or rods), which gathered into clusters. Figure 6 shows a side-by-side comparison of TEM and SEM results. FTIR analysis once more confirmed the formation of these tubes, with a B-N-B peak around 800 and B-N at 1300 (Figure 7). EDX was able to show that Mg was also present in the sample (Figure 8).

The reaction described above was replicated and called GR-04. The crude product was then purified using a modified purification method. Nitric acid was used originally, however, due to its corrosiveness, the structure of the tubes was not able to remain intact. It became necessary to replace nitric acid with hydrochloric acid. After purification, FTIR data of the product was obtained. The spectra showed that the usual BNNT products remained, as can be seen in Figure 9.



Figure 9. FTIR spectra obtained for GR-04 after purification. Usual BNNT peaks were observed.

TEM images were also obtained (Figure 10), and these showed tubes were still present in the sample, gathered in small clusters, and somewhat clearer than the original tubes. However, as is evident in the images, a large amount of impurities remained.

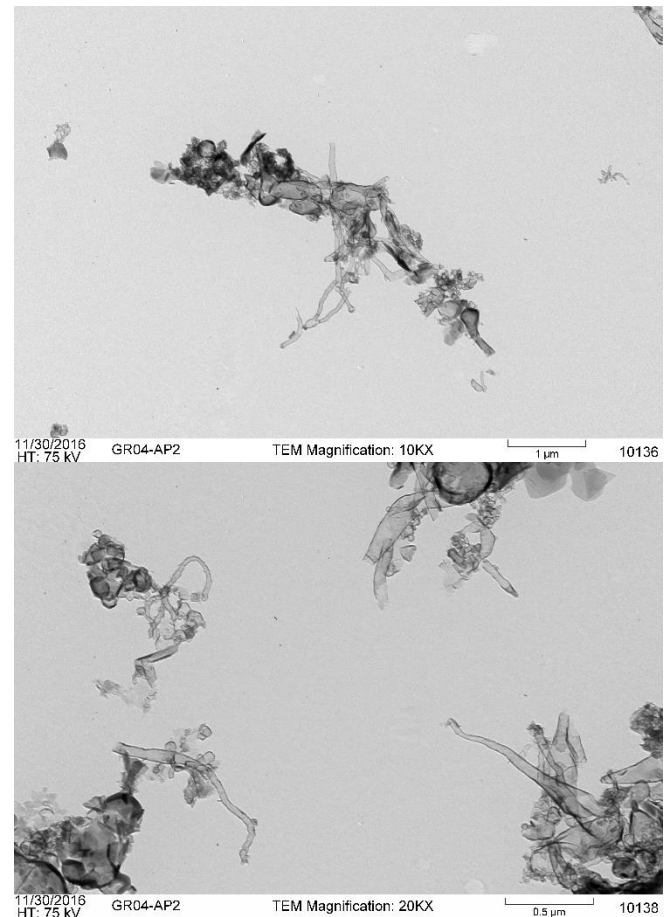


Figure 10. TEM images obtained for GR-04 after purification. Although tubes appear to be clearer and gather in clusters, impurities remain visible in sample.

**CONCLUSIONS AND FUTURE WORK.** In summary, TEM, SEM, FTIR, and EDX analyses confirmed the formation of BNNTs and their possible intercalation with magnesium. EDX showed magnesium was present in the product sample, while TEM allowed us to see hair-like structures on the surface of the tubes, indicating intercalation had occurred. However, further characterization of the product must be performed in order to assess exactly how magnesium is attached to the BNNT structure.

The product also underwent treatment with acid in order to be purified. Various methods were tried and discarded due to their corrosiveness and inability to maintain the tubes' structure. It was found that treatment with HCl kept the tubes intact. FTIR data obtained after purification confirms the presence of tubes in the sample, as the expected BNNT peaks are evident. TEM images also confirm the presence of the tubes and the integrity of their structure. However various impurities remain visible.

In the future, additional reactions will be performed in order to see if results can be duplicated or improved upon by slightly altering reaction conditions like the quantity of reactants or the reaction length. Furthermore, the purification method established requires further investigation. If intercalation is successful, a combination reaction with lithium and magnesium will be performed for BNNT intercalation with both metals.

#### **ACKNOWLEDGMENTS**

Thank you to my faculty mentor, Dr. Narayan Hosmane, for graciously allowing me to work in his lab.

Thank you also to my lab partners Gabriela Fuentes and Tu Nguyen for their help in conducting these experiments.

Finally, thank you to Lori Bross, Jue Gong, Timothy Perkins, Michael Figora, Okan İçten, and Nathanielle Guevarra for their invaluable contributions to this project.

#### **AUTHOR INFORMATION**

##### **Roxana Moraga**

Department of Chemistry and Biochemistry, Northern Illinois University.

Email: z1721051@students.niu.edu

##### **Narayan S. Hosmane, PhD.**

Department of Chemistry and Biochemistry, Northern Illinois University.

Email: hosmane@niu.edu

#### **REFERENCES**

Ciofani, G.; Danti, S.; Genchi, G.; Mazzolai, B.; Mattoli, V. Boron Nitride Nanotubes: Biocompatibility and Potential Spill-Over in Nanomedicine. *Boron Nitride Nanoparticles*. **2013**, *9*, 1672-1685.

Denis, P. Improving the Chemical Reactivity of Single-Wall Carbon Nanotubes with Lithium Doping. *J. Phys. Chem.* **2011**, *115*, 20282-20288.

Feng, L.; Liu, Y.; Zhao, J.; Ding, Y. Theoretical Study on the Encapsulation of Li Atoms inside Boron Nitride Nanotubes: Physical Properties and Catalytic Reactivity for the Oxygen Reduction Reaction. *J. Phys. Chem.* **2014**, *118*, 30325-30332.

Golberg, D.; Bando, Y.; Kurashima, K.; Sato, T. Nanotubes of Boron Nitride Filled with Molybdenum Clusters. *J. Nanosci. Nanotechnol.* **2001**, *1*, 49-54.

Ricotti, L.; Fujie, T.; Vazão, H.; Ciofani, G.; Marotta, R.; Brescia, R. Boron Nitride Nanotube-Mediated Stimulation of Cell Co-Culture on Micro-Engineered Hydrogels. **2013**, *8*(8): e71707.

