Synthesis of Lithium Intercalated Boron Nitride Nanotubes

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Synthesis, characterization and application of Lithium intercalated boron nitride nanotubes


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

ABSTRACT: Synthesis of Lithium Intercalated Boron Nitride Nanotubes (Li-BNNT) was conducted in an attempt to gain access to their promising applications for electronics, lithium batteries, hydrogen storage, and supercapacitors. Through a series of reactions pure nanotubes intercalated with lithium are expected to show in the product. A variety of reactions are engineered to create optimal conditions for the product and the reaction is conducted at 700º or 800ºC with zinc acting as a catalyst. The products were then purified using hexane and characterized using Transmission Electron Microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy-dispersive X-ray Spectroscopy (EDX). Further purification, functionalization, and application will be performed to access the promising applications that Li-BNNT offers.

INTRODUCTION: Boron nitride nanotubes (BNNT) have successfully been produced very few times. This is astounding when looking at their vast and extraordinary capabilities. BNNT’s have amazing chemical stability and heat resistance when compared to carbon nanotubes (CNT). They also possess a high Young’s modulus and have incredible piezoelectric properties. Even with these amazing qualities there has been limited research involving BNNT because of their difficulty to functionalize and synthesize in large quantities. The research that has been conducted thus far is inspiring and exemplifies BNNT’s versatility. BNNT’s being more stable than the CNT’s, offer a great alternative to nanomedicine and production of nanomaterials. The CNT doping of lithium produces nanotubes that are more conductive, more reactive, and are able to bond to functional groups better. When concentrating on the intercalation of lithium in BNNT, it is important to look at the isoelectronic CNT as an example, since there is no research currently that gives an indication as to what intercalation of lithium might do in BNNT. Lithium intercalation could possibly enhance BNNT’s applications. Supercapacitors and lithium ion batteries hold a promising future in clean energy, thus being able to synthesize Li-BNNT, could boost supercapacitors abilities and maximize its energy capabilities.

MATERIALS AND PROCEDURE: All the chemicals used in this study were obtained from Sigma Aldrich and were used as such without further purification, unless otherwise specified. Of the several reactions conducted in an effort to obtain Li-BNNT the reactants include: LiBH₄, NH₄BF₄, NaN₃, and Zn dust. Of these reactants there are a few which are corrosive and can cause severe eye damage (NH₄BF₄), emit flammable gasses (LiBH₄), and toxic to skin (NaN₃). An MTI furnace, GSL series model, OTF-1200X is used for firing the reactant in the pressure vessel. Transmission electron microscopy (TEM), Scanning Electron Microscopy (SEM), Fourier Transform Infrared Spectroscopy (FTIR), and Energy-dispersive X-ray Spectroscopy (EDX), are used for characterization of the product. Li-BNNT intercalated was produced through a series of two trial reactions, choosing the reaction scheme which optimizes the yield. We used the following reaction scheme for the synthesis of Li-intercalated BNNT with Zn as a catalyst:

\[
2\text{Li(BH}_4\text{)}_{(s)} + 2\text{NH}_4\text{BF}_4\text{(s)} + 8\text{NaN}_3\text{(s)} \stackrel{Zn}{\rightarrow} 2[(\text{BN})_{x}\text{-Li-(BN)}]_{(s)} + 11\text{N}_2\text{(g)} + 8\text{H}_2\text{(g)} + 8\text{NaF}_{(s)} \quad (1)
\]
We used the following reaction scheme for the synthesis of Li-intercalated BNNT without Zn as a catalyst:

\[
2\text{Li(BH}_4\text{)}_\text{(s)} + 2\text{NH}_4\text{BF}_4\text{(s)} + 8\text{NaN}_3\text{(s)} \rightarrow 2[(\text{BN})_x\text{-Li-(BN)}_x\text{]}\text{(s)} + 11\text{N}_2\text{(g)} + 8\text{H}_2\text{(g)} + 8\text{NaF}\text{(s)}
\]  

(2)

For each scheme the reactants were accurately weighed inside a glove box which maintained an argon environment. The reactants were then finely powdered using a pestle and mortar. The contents are then transferred into a pressure vessel which could withstand 6000 atm pressure and 700ºC/800ºC. The pressure vessel is tightly screwed with the contents inside and ensured a moisture free reaction atmosphere. The pressure vessel is then removed out of the glove box and further tightened using suitable mechanical devices. The pressure vessel is then transferred to the MTI furnace and the temperature programming is done according to table 1. Temperature conditions were also varied, with some reactions performed at 700ºC and others at 800ºC.

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

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

PURIFICATION: The purification method has since been renewed, beginning with the grinding of the product with a mortar and pestle that is place in a Erlenmeyer flask with a 150 ml of 95% ethanol and sonicated for an hour. The product is then placed in a round bottom flask and dried through use of rotovap, after drying the product is diluted with DI H2Ol. Once this step has been completed the product is laid in a oil bath combined with a hot plate and condenser and heated for three hours staying under 90ºC. The final step of purification involves to vacuum filtration of the solution and the filtrate being left to dry overnight in the oven.

RESULTS AND DISCUSSION: The reaction was conducted four times, three at 800ºC and one at 700ºC. The reactions conducted at 800ºC would melt the gasket which would then contaminate the product. The product retrieved from the reaction conducted at 700ºC, allowed the gasket to remain intact and was taken for further characterization due to its white color and abundance weighing a little over 4 grams. The vessel in which the reaction is ran in was also refurbished to increase the quality and quantity of our product. This gave us our first grey-white flaky product that was nickname “GRB1”, this product was analyzed using transmission electron microscopy (TEM) producing images showing tubes (shown in images 1-6). The images also show other dark structures believed to be impurities within/surrounding the lithium intercalated boron nitride nanotubes. The sample will be taken for SEM which will hopefully
show a myriad of tubes similar to the TEM. Boron is difficult to be analyzed through EDX due to its low elemental weight, but the EDX will be helpful in determining the possible impurities believed to be in the product, such as NaF. Finally, fourier transform infrared spectroscopy also confirmed that the product did contain boron nitride nanotubes and the important B-N bond, this can be seen in image 7. The purification method should show a significant difference in all the previously aforementioned characterization methods and as testing occurs it will be easier to compare the product before and after purification. The vessel in which the reaction is ran in was also refurbished to increase the quality and quantity of our product, this gave us white-marble sized product we dubbed “GRB2”. GRB2 was taken for TEM and these images can be seen in images 8-16. The GRB2 also confirmed to have the important B-N-B bond which can be seen at peak 816 (image 17). Finally, it was difficult to get high resolution TEM and SEM so instead to prove the presence of lithium a water test was done showing regular BNNT being insoluble in water and are assumed Li-BNNT bubbling and dissolving in water indicating that lithium is in our product (image 18). The product was also burned over a fire, this fire showed a large red flame indicating lithium is in the product, as lithium burns red and it has flicks of green which indicated boron was present as well (image 19).

Image 1: TEM of unpurified product showing tubes and various other impurities
Image 2: TEM of unpurified product showing tubes with possible intercalation.

Image 3: TEM of unpurified product, mass of interwoven tubes, cages and impurities.
Image 4: TEM of unpurified product, Very long possibly intercalated tubes.

Image 5: TEM of unpurified product, astounding three-dimensional cage
Image 6: TEM of unpurified product, large view of tube that is possibly intercalated.

Image 7: GRB1 FTIR
*This tube in the center of the image grew right in front of our eyes!
Image 17: GRB2 FTIR

![GRB2 FTIR graph](image_url)

Image 18: Water test

*The left is Li-BNNT and the right is regular BNNT*
CONCLUSIONS:

The results obtained indicate possible intercalation of Lithium in the BNNT structure, and the definite formation of nanotubes as shown in the various character analyses TEM, and will be proven through SEM, FTIR, and EDX. However, further characterization of the product must be performed in order to examine if/how lithium is attached to the BNNT structure. The product was also purified through a three step mechanism which produced transparent tubes and significantly less impurity in the images, such as blobs or nanoparticles in the nanotubes, but characterization needs to be done on the newest reaction.

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Cited work:


