Improved Crystallinity of B_4C Nanosheets from Liquid Phase Exfoliation

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Introduction

Boron carbide (B_4C) is a ceramic material known for its incredible hardness. Liquid exfoliation of B_4C into nanosheets by bath sonication has been proven to work in making this material into a 2D material. This project was aimed at improving the method of synthesizing these nanosheets to get a better concentration of nanosheets and higher quality products. This project will compare the results of this experiment, using DI water, and the results of Ref. [1], using isopropyl alcohol (IPA).

Approach

Bath Sonication

- B_4C was dissolved into DI water and put into a vial that hangs inside of a water bath. Sound waves pass through the body of water inside of the bath and exfoliate the material. Liquid-phase exfoliation is normally used for layered materials. B_4C is not a layered material, this is the innovation of the project.

Gathering data

- The B_4C samples were characterized via Raman spectroscopy to gather optical images and spectra plots to judge crystallinity. High carbon bonding peaks in the Raman spectra would give an indication of poor crystallinity.

Methods

Liquid Exfoliation

- 0.4g of powdered bulk B_4C particles are put in a vial with 6 mil DI water as a solvent and suspended in a sonication bath. The bath exfoliates the particles into 2D nanosheets. This sonication process is repeated for several hours to get different samples to see how long the sonication process needs to take place to get the best quality nanosheets.

Characterization

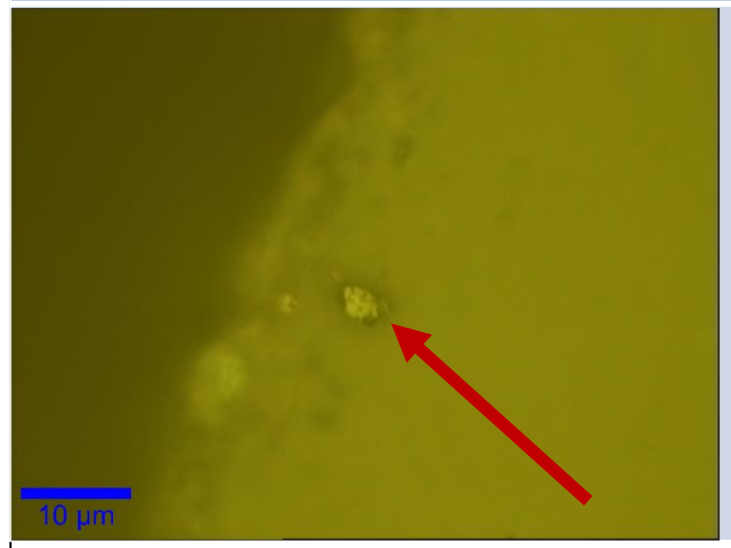
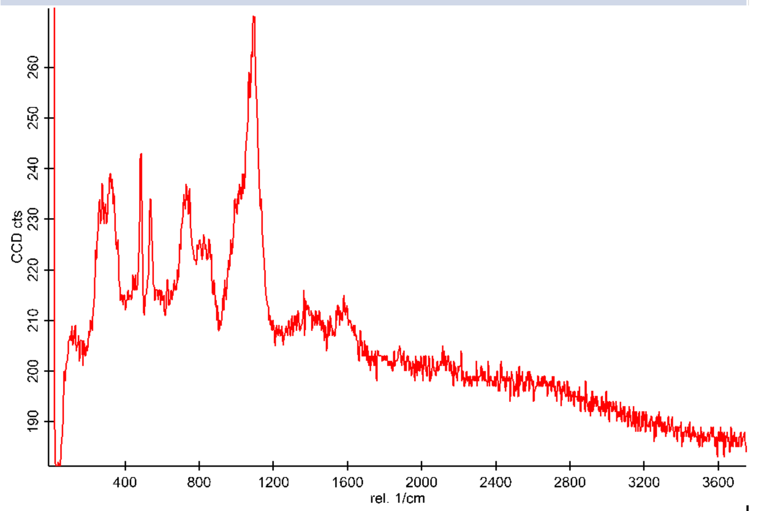
- The B_4C vials that were sonicated were put into a centrifuge to then only collect the nanosheets in the vials and not the bulk particles that have gathered onto the bottom of the vials. These nanosheets were put onto a sapphire (Al_2O_3) substrate by a spin coating method. These substrates were then used to transport the nanosheets to be characterized by Raman spectroscopy. Sapphire substrates will not interfere with the peaks given by the sample in the Raman spectra.

Results and Analysis

B_4C Sonication Time	Ratio of Samples with Poor Crystallinity Versus Total Sample Size
3 hr	2/28 ≈ 7.1428571%
4 hr	1/32 = 3.125%
5 hr	0/30 = 0%

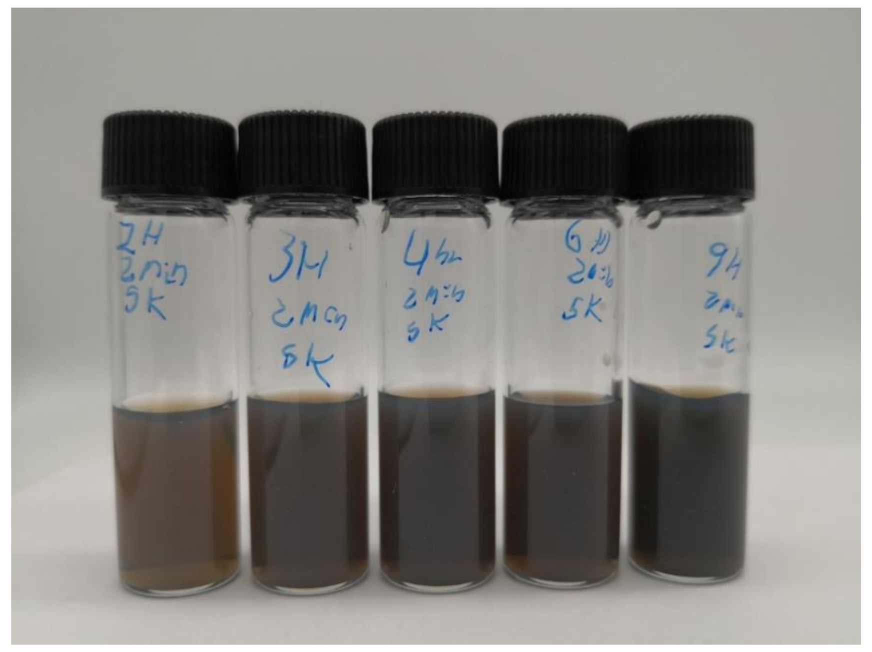
Table showing sample crystallinity versus sonication time.

B_4C Nanosheets (3hr example)

Optical image	Raman Spectra
	

10µm scale bar (bottom left of optical image), nanosheet in center of image. Spectra x-axis is rel. 1/cm and y-axis is CCD cts.

B_4C Nanosheets (in solution)



2,3,4,6,9 hr sonication time B_4C Nanosheets in solution

Obstacles

- Samples of B_4C nanosheets in their vials would degrade over a period of a month. Because of this, the 2, 6, and 9 hr samples were not used.
- The process of synthesizing the B_4C nanosheets and to search for them on the substrates is time consuming because of limitations of automation.
- Purity of samples is hard to control.

Conclusions

- Crystallinity improved overall versus Ref [1]. After 5 hours of bath sonication almost no defects were detected in the samples.
- Using water as a solvent prevented more defects than used with IPA.
- DI water is beneficial for making the nanosheets have better crystallinity, but it is poor in keeping the products stable while in the solution.
- Big thank you to all the staff, students, and faculty that made this project happen! And, to W.L. Gore for sponsoring this project!

Reference

1. Guo, Yuqi et al. "Exfoliation of Boron Carbide into Ultrathin Nanosheets." Nanoscale 13.3 (2021): 1652–1662. Web.
2. Domnich, V. et al. (2011). Boron Carbide: Structure, properties, and Stability under Stress. *Journal of the American Ceramic Society, Vol (94),* 10.1111/j.1551-2916.2011.04865.x
3. Liu X, Zheng M, Xiao K, et al. Simple, green and high-yield production of single- or few-layer graphene by hydrothermal exfoliation of graphite. Nanoscale 2014, 6: 4598–4603.
4. Lv, H. et al. (2012). Nano-boron carbide supported platinum catalysts with much enhanced methanol oxidation activity and CO tolerance. *Journal of Materials Chemistry, Vol.(22),* Pages 9155-9160. 10.1039/c2jm30538k
5. Mu, S., et al. (2016). Nano-size boron carbide intercalated graphene as high performance catalyst supports and electrodes for PEM fuel cells. *Elsevier, Vol (103)* Pages 449-456. 10.1016/j.carbon.2016.03.044
6. Ni, G., Li, G., Boriskina, S. et al. Steam generation under one sun enabled by a floating structure with thermal concentration. Nat Energy 1, 16126 (2016). https://doi.org/10.1038/nenergy.2016.126
7. Shang, W. & Deng, T. Solar steam generation: Steam by thermal concentration. *Nat. Energy* **1,** 16133 (2016).
8. Tian, Z., et al. (2019). Crystalline boron nitride nanosheets by sonication-assisted hydrothermal exfoliation. *Journal of Advanced Ceramics, Vol. (8),* Pages 72-78. 10.1007/s40145-018-0293-1
9. Wisnuwijaya, I. R., Purwanto, A., & Dwandaru W. S. B. (2017). UV-Visible Optical Absorbance of Graphene Oxide Synthesized from ZincCarbon Battery Waste via a Custom-Made Ultrasound Generator based on Liquid Sonication Exfoliation Method. *Makara Journal of Science*, *Vol. (21)*, page 175- 181. 10.7454/mss.v21i4.6752