Exfoliation of Two-Dimensional Boron from non-van der Waals Crystals

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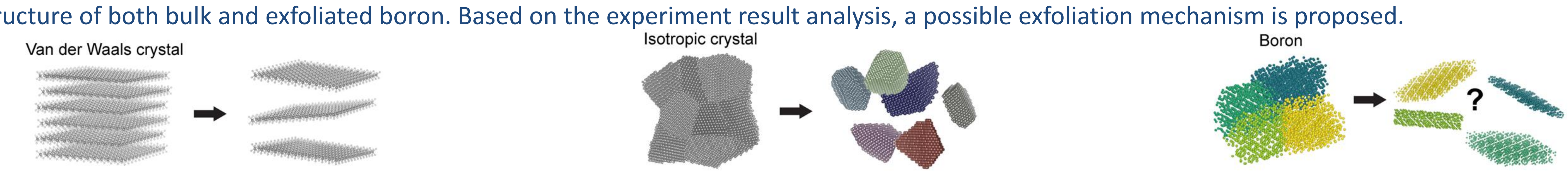
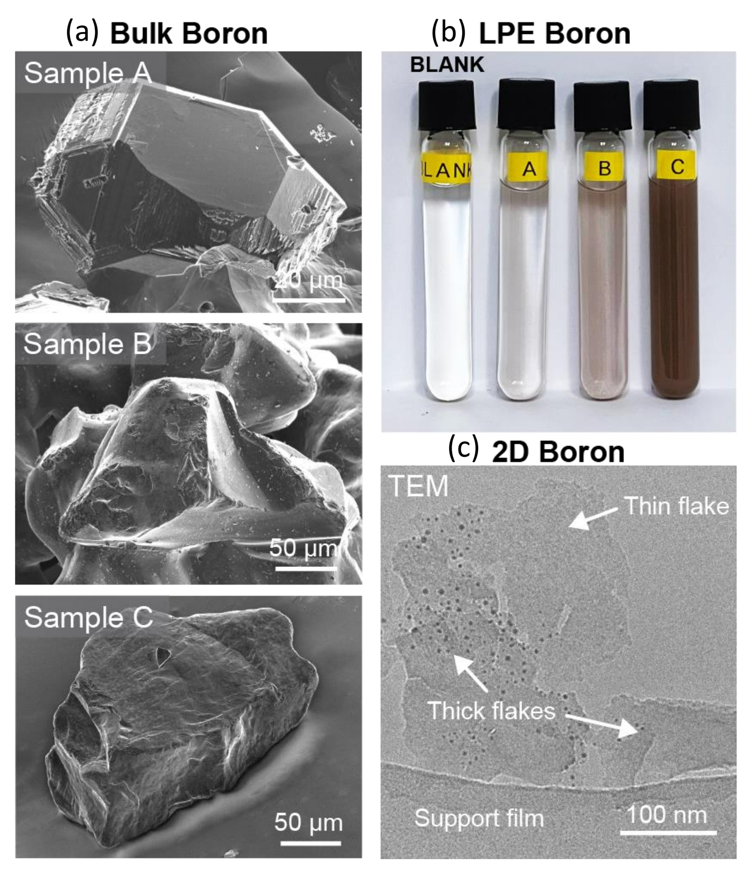
Introduction

Inspired by the discovery of borophene – graphene-like structure made from boron atoms, in-situ grown on flat surfaces in ultra-high vacuum – several reports demonstrated synthesis of two-dimensional boron flakes (2D-boron) via liquid-phase exfoliation from the bulk boron crystals, and explored their physical and chemical properties [1-2]. While the other 2D materials are exfoliated from layered van der Waals crystals, 2D boron is synthesized from the covalently-bonded bulk crystal, without any preferential, cleavable crystal direction. The synthesis would require breaking of the covalent bonds, and neither the exfoliation mechanism nor the atomic structure of the resulting 2D boron is understood. In this work, we explored the liquid-phase exfoliation of boron bulk and studied the chemical and atomic structure of both bulk and exfoliated boron. Based on the experiment result analysis, a possible exfoliation mechanism is proposed.



Liquid-phase exfoliation of Boron



We used three different precursor as starting material for LPE.

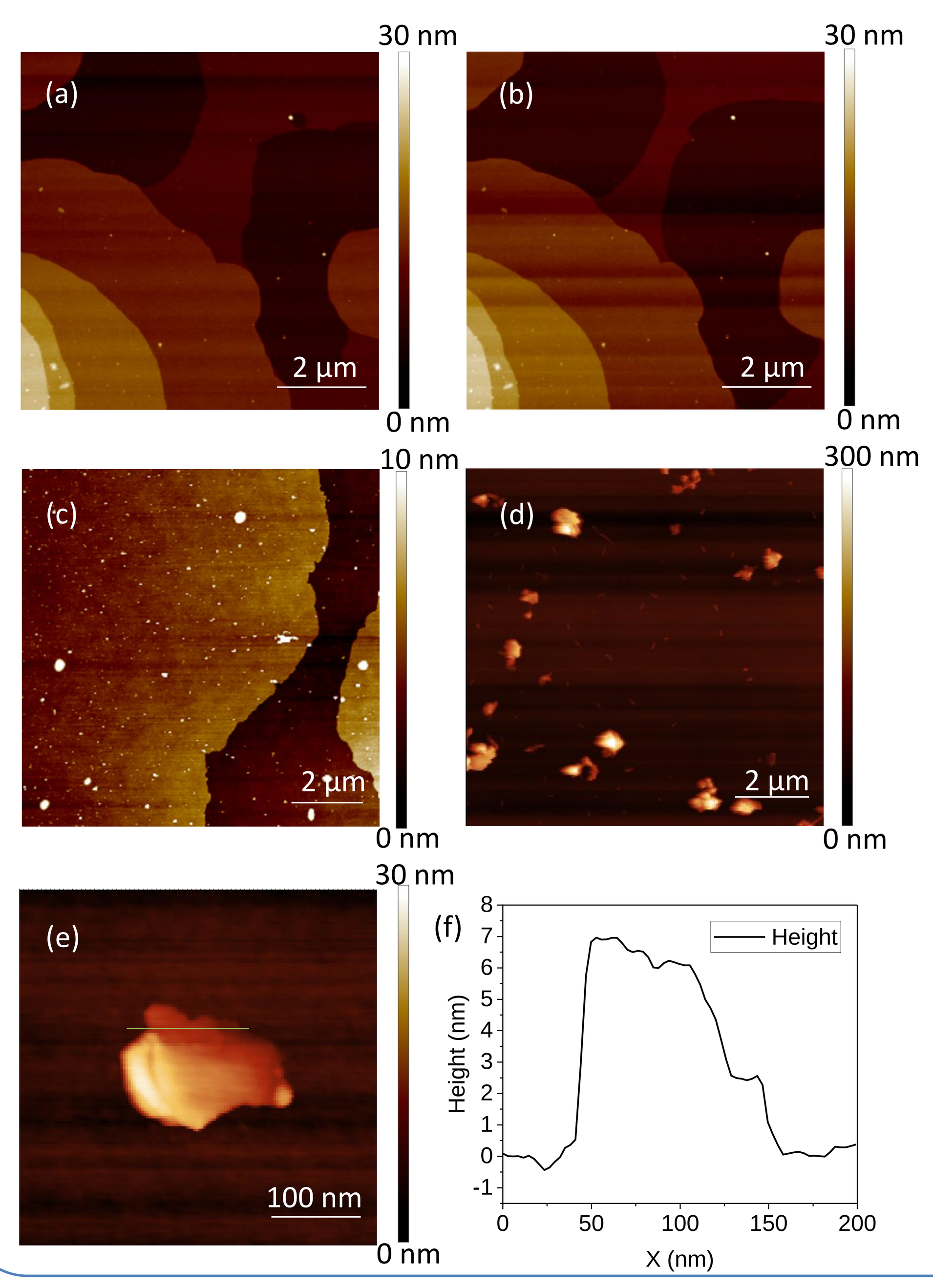
Sample A: Boron pieces, large grain size

Sample B: Boron pieces, small grain size

Sample C: Boron powder, small grain size

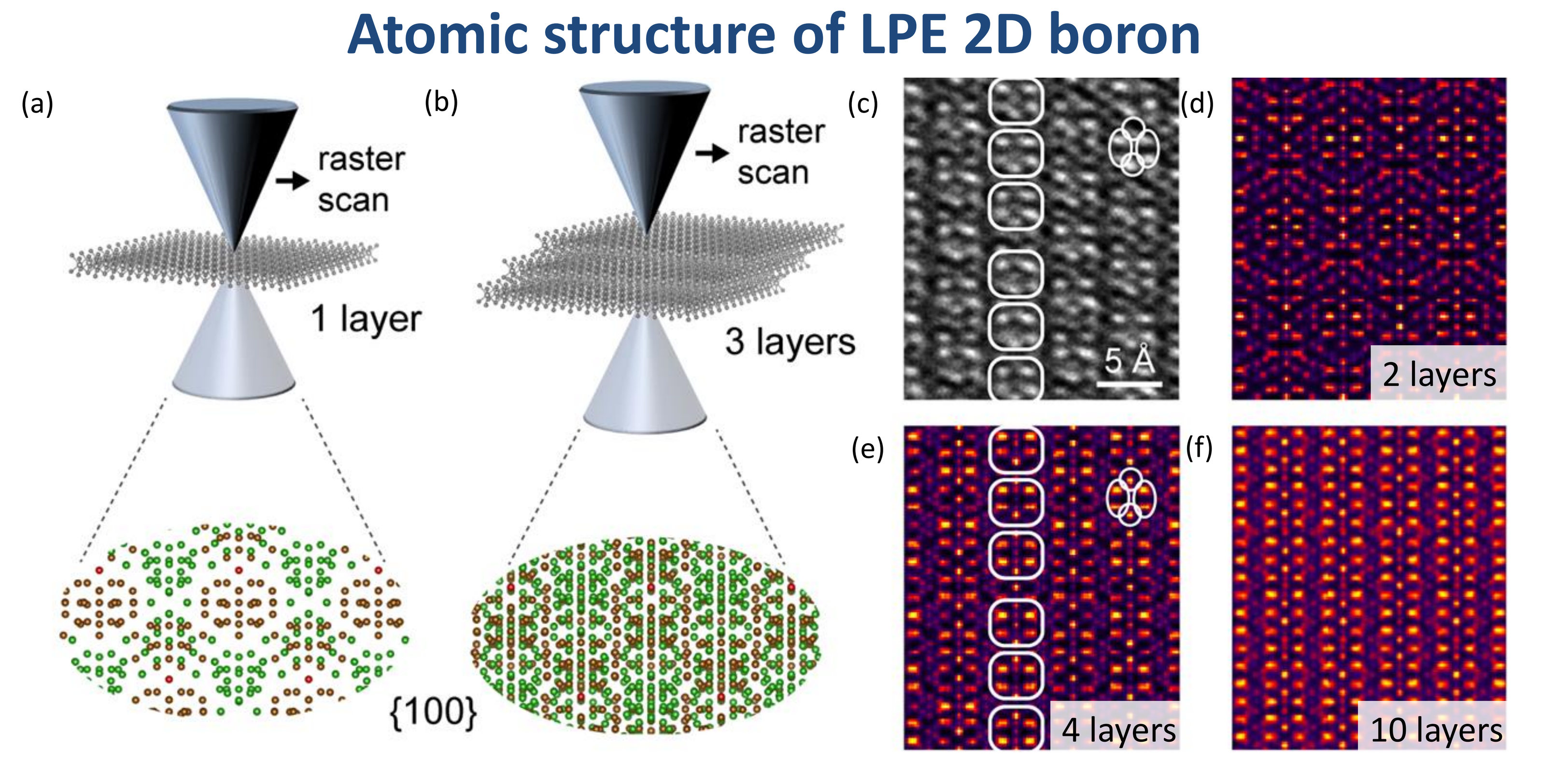
2D boron observed

Flakes found in LPE boron products



- Artifacts (patches of dried solvent or surfactant) has been found In the LPE boron products.
- Artifacts could be single layer or multilayer with flat surface as figures (a-b) show.
- Most of the artifacts can be removed by annealing. Figures (c-d) show LPE boron products before and after annealing, respectively.
- The 2D boron flakes are usually not very flat. Their thickness could be a few nanometers to hundreds of nanometers. Figures (e-f) show a typical boron flake with a wedge shape.

Atomic structure of LPE 2D boron

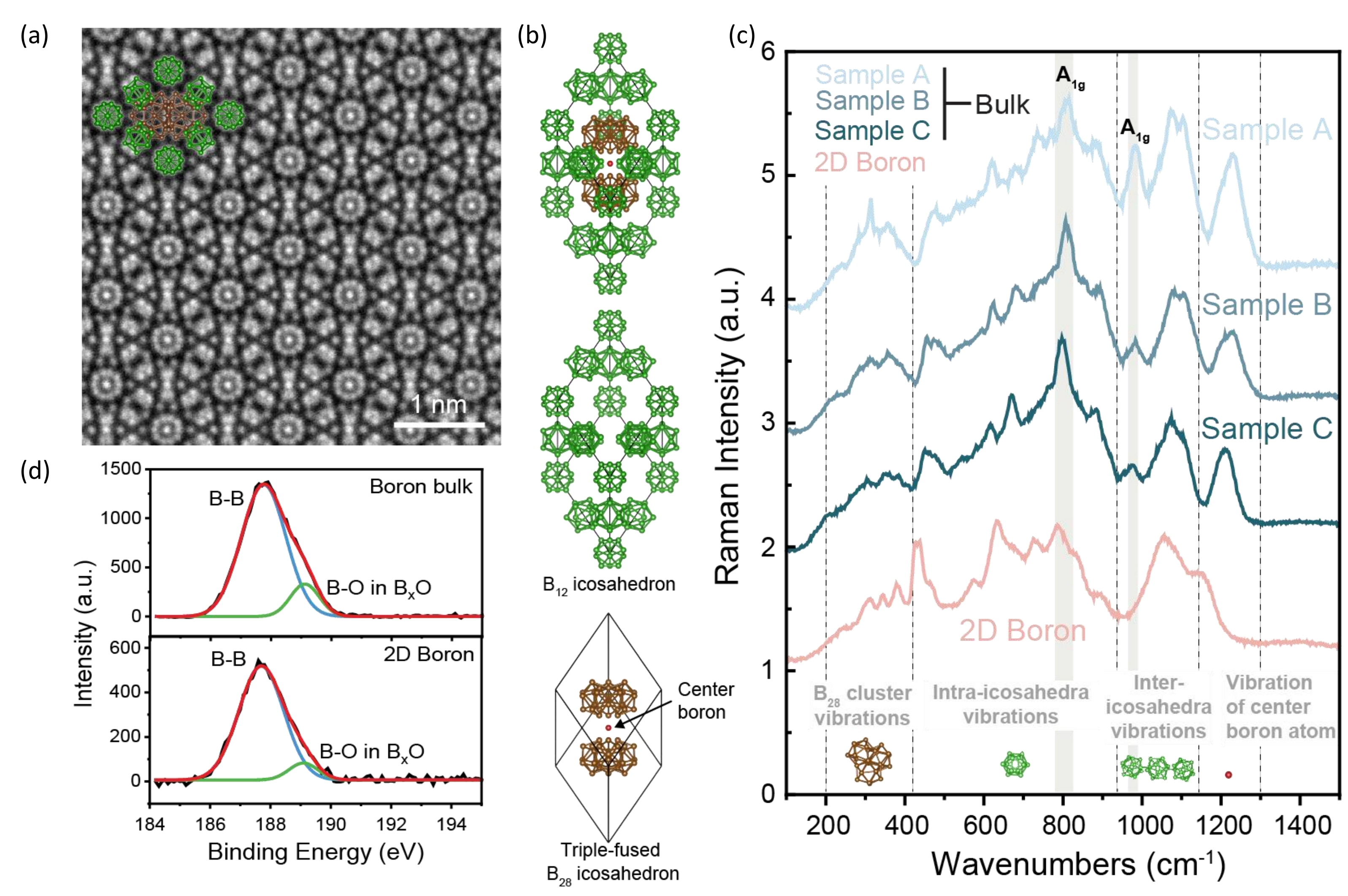


STEM images of LPE 2D boron determined

1. The thickness of 2D boron flakes.
2. The orientation and tilt angle of the flakes.

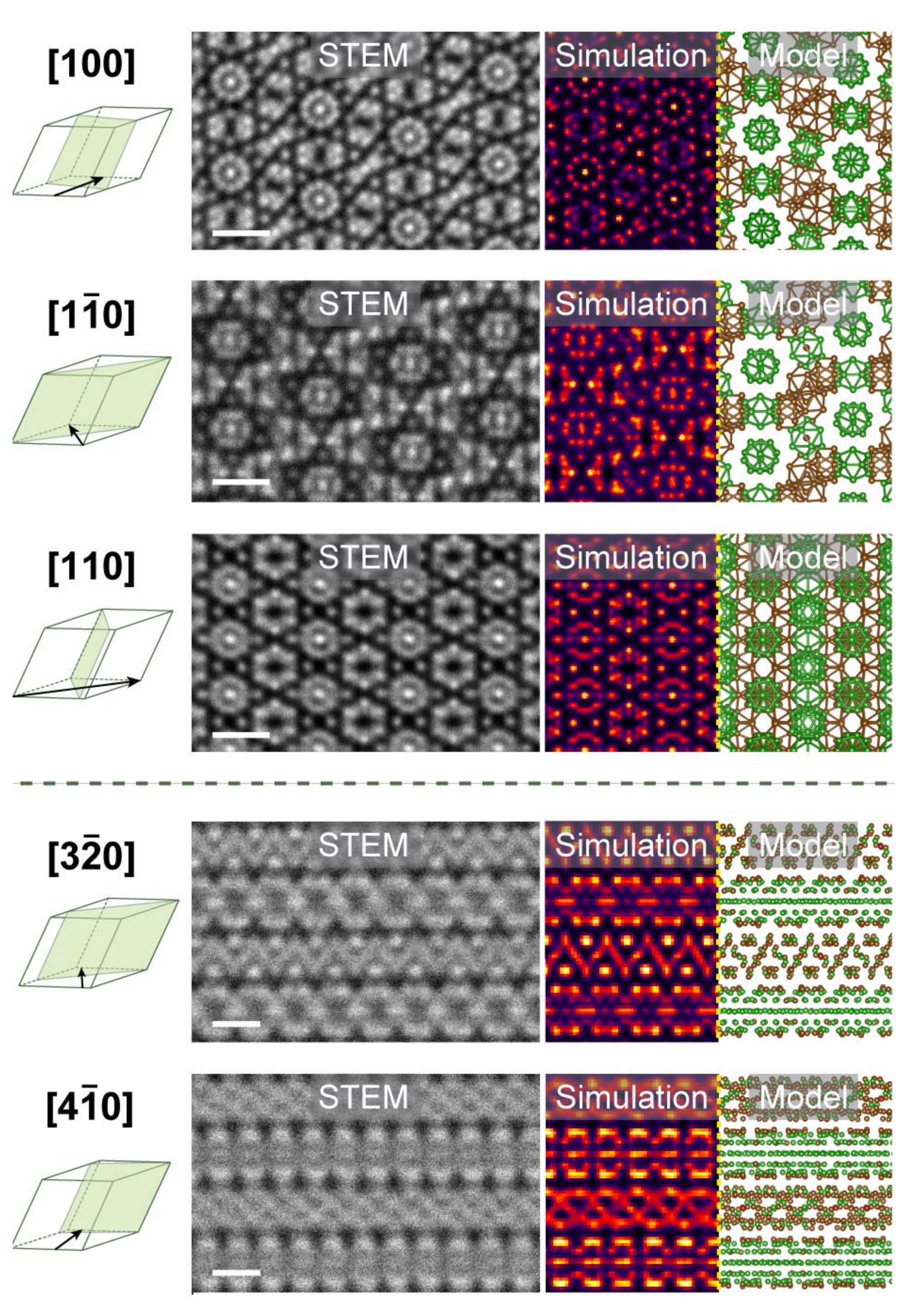
Figure (c) shows a 4-layer 2D boron with {100} plane in perpendicular angle.

Phase and elemental characterization of bulk boron and LPE boron



- STEM image (figure (a)) and Raman spectroscopy of the bulk boron (figure (c)) revealed their atomic structure to be β-rhombohedral boron[3] as figure (b) shows.
- Raman peaks of Samples A is much sharper and more obvious than Samples B and C, indicating it has higher crystallinity.
- XPS of B1s before and after LPE (figure (d)) indicated there are no obvious oxidation of boron or phase change during the LPE process.
- The Raman spectrum of the exfoliated 2D boron (figure (c)) retain the overall profile of bulk boron, but contains slight peak shifts, new and reduced peaks, indicating the breaking of symmetry in unit cell after LPE.

Atomic-structure of bulk β-rhombohedral boron



- STEM images along the [001], [110] and [1$\bar{1}$0] orientations of the bulk boron shows the B_{12} icosahedron columns. This feature can be used to identify the β-rhombohedral phase.
- STEM images along [3$\bar{2}$0] and [4$\bar{1}$0] orientations give the appearances of seemingly layered structures.
- Within these planes, we also found defects in the form of twin boundaries and stacking faults.
- The bulk structure and its defects could explain the exfoliation mechanism of boron.

Conclusion

We explored the liquid-phase exfoliation of 2D boron from different types of bulk crystals. We found that the crystallization and size of the bulk material strongly affects the concentration and particle size of LPE products. Using Raman spectroscopy and STEM analysis, we realized both the bulk source and the resulting 2D boron are β-rhombohedral. By analysis and modeling of the STEM data, we revealed the structure of bulk boron and the orientation and the thickness of the sonicated boron flakes. Comparing the structure of bulk boron and 2D boron, we proposed a possible exfoliation mechanism based on the defects in bulk. The understanding of 2D-boron could inspire strategies for discovery of a new class of 2D materials that do not require van der Waals crystals.

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2. Ranjan, P.; Sahu, T. K.; Bhushan, R.; Yamijala, S.; Late, D. J.; Kumar, P.; Vinu, A., Freestanding Borophene and its Hybrids. Advanced Materials 2019, 31 (27), 1900353
3. Werheit, H.; Filipov, V.; Kuhlmann, U.; Schwarz, U.; Armbrüster, M.; Leithe-Jasper, A.; Tanaka, T.; Higashi, I.; Lundström, T.; Gurin, V. N.; Korsukova, M. M., Raman Effect in Icosahedral Boron-Rich Solids. Science and Technology of Advanced Materials 2010.