Hydrogen effect in the synthesis of boron nitride nanostructures

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Introduction

Boron nitride (BN) nanostructures can be synthesized in various forms, such as nanotubes, nanocages, and nanoflakes. However, details of the synthesis process in atomic level are still not clear. For example, hydrogen is found very important for the synthesis of BNNT, as reported in previous experimental studies:

- Addition of hydrogen to the reactant gases during the plasma synthesis of BN materials is crucial for achieving high-quality, high-yield growth of BNNTs. [1]
- Our collaborators in PPPL also observed a increased ratio of single wall BNNT to multi-wall BNNT when H_2 is introduced in hot plasma.

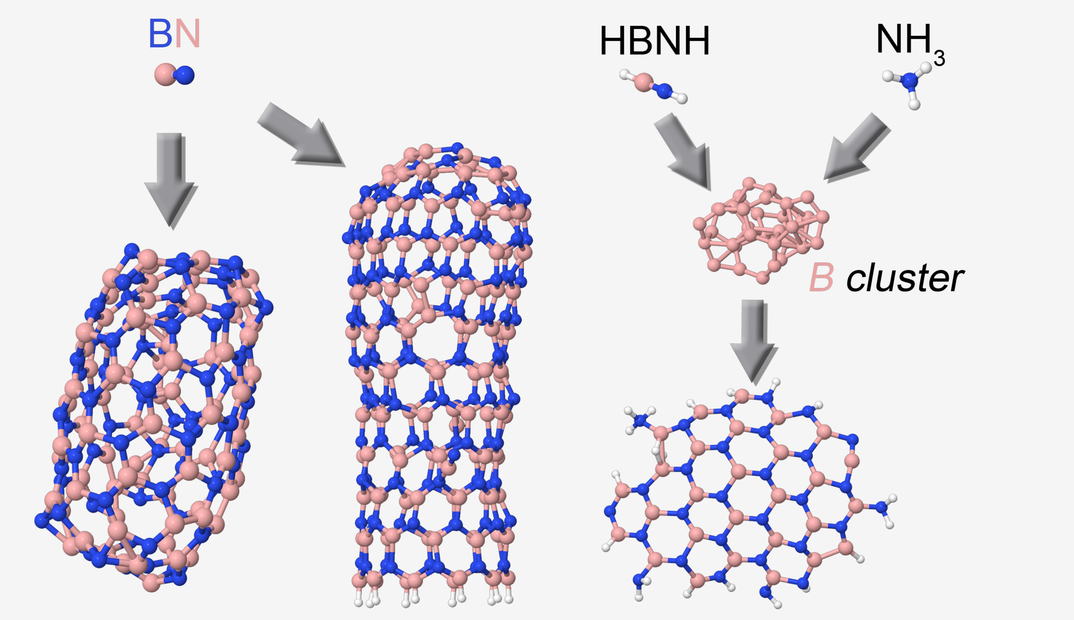


Figure 1. Different BN nanostructures created in simulation of bombardment of feedstock molecules toward targets.[2]

We have successfully simulated the growth of BN nanocage, nanoflakes, and BNNTs by bombardment of different feedstock molecules to the target, using quantum classical molecular dynamics approach.[2] In current work, we will adopt similar approach, trying to unveil how hydrogen affects the BN structure during the synthesis in plasma volume.

We studied the hydrogen effect in the BN nanostructure synthesis from the following aspects:

- Size of B cluster:
  - B_{36}, B_{72}, B_{96}, B_{144}, B_{192}
- Feedstock species:
  - H, NH, NH_2, NH_3
- Temperature:
  - 1500K, 2000K, 2500K

Creation of c-BN nanocrystals

c-BN can be created in following conditions

1:
- Boron cluster of size > B_{144}
- Feedstock: N,NH, NH_2
- Temperature = 2000K

2:
- Pre-formed double-wall BN nanocages
- Feedstock: H
- Temperature = 2000K

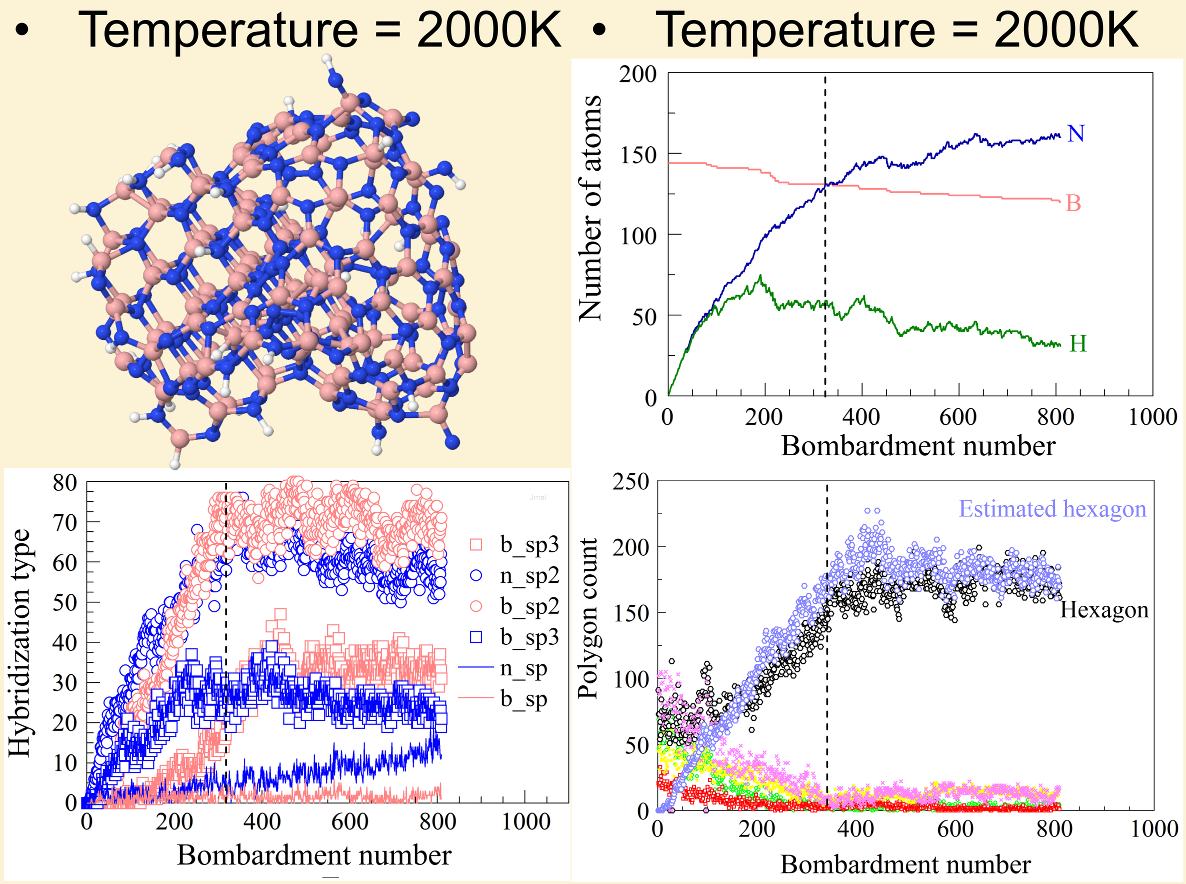


Figure 2. c-BN nanocrystal created by bombarding B144 cluster with NH molecules at 2000K. Statistics of atom number count, hybridization type of B and N atoms, and polygon count are shown with the structure. The dashed line in the plots represents the bombardment number when c-BN nucleus is observable.

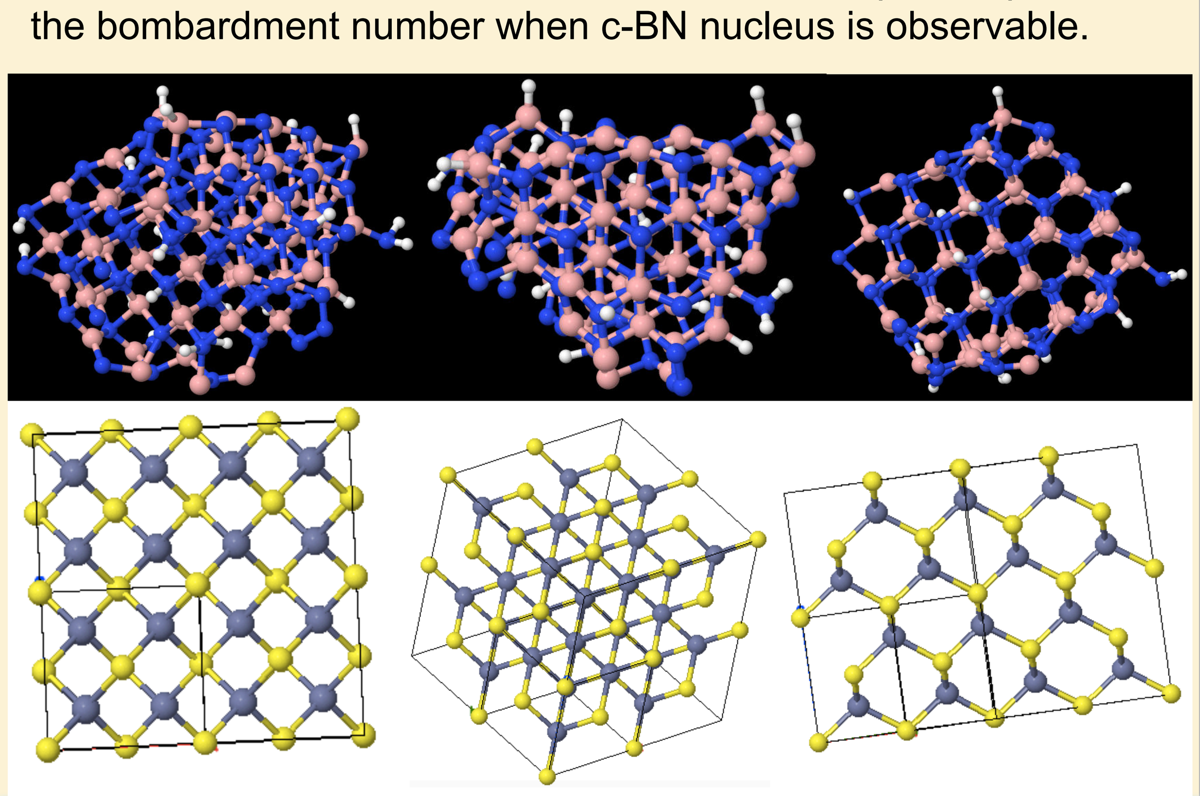


Figure 3. Comparison of created BN nanocrystal with cubic ZnS in three views,[3] confirming the BN nanocrystal is cubic.

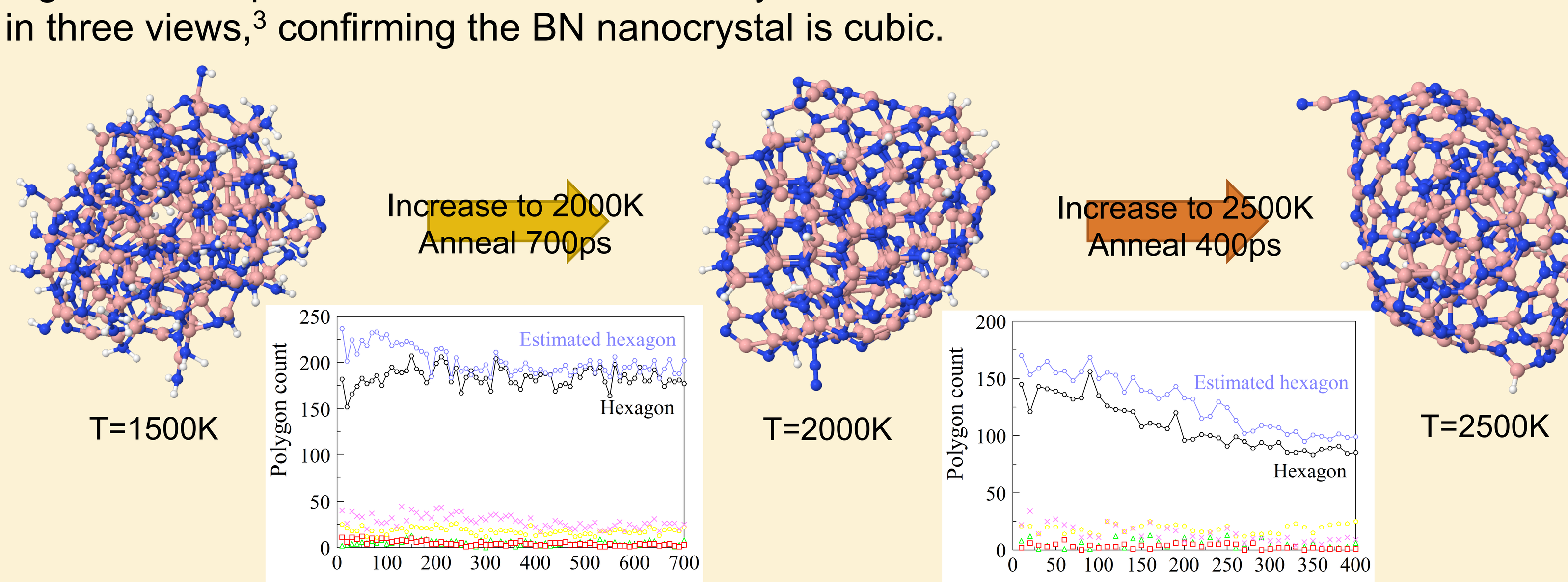


Figure 4. Transformation of BN nanostructure from amorphous cluster at 1500K to c-BN at 2000K, and finally to nanocage at 2500K. Plots show the evolution of polygon number.

- c-BN can also be created by transformation of BN structure at 2000K.
- 1500K: amorphous cluster
- 2000K: cBN nanocrystal
- 2500K: BN nanocage (can be single-wall or double-wall)

Creation of BN sw-cage

B96 cluster + N atoms:

double-wall BN cage (4 out of 5 samples)

B96 cluster + BN atoms:

single-wall BN cage (4 out of 4 samples)

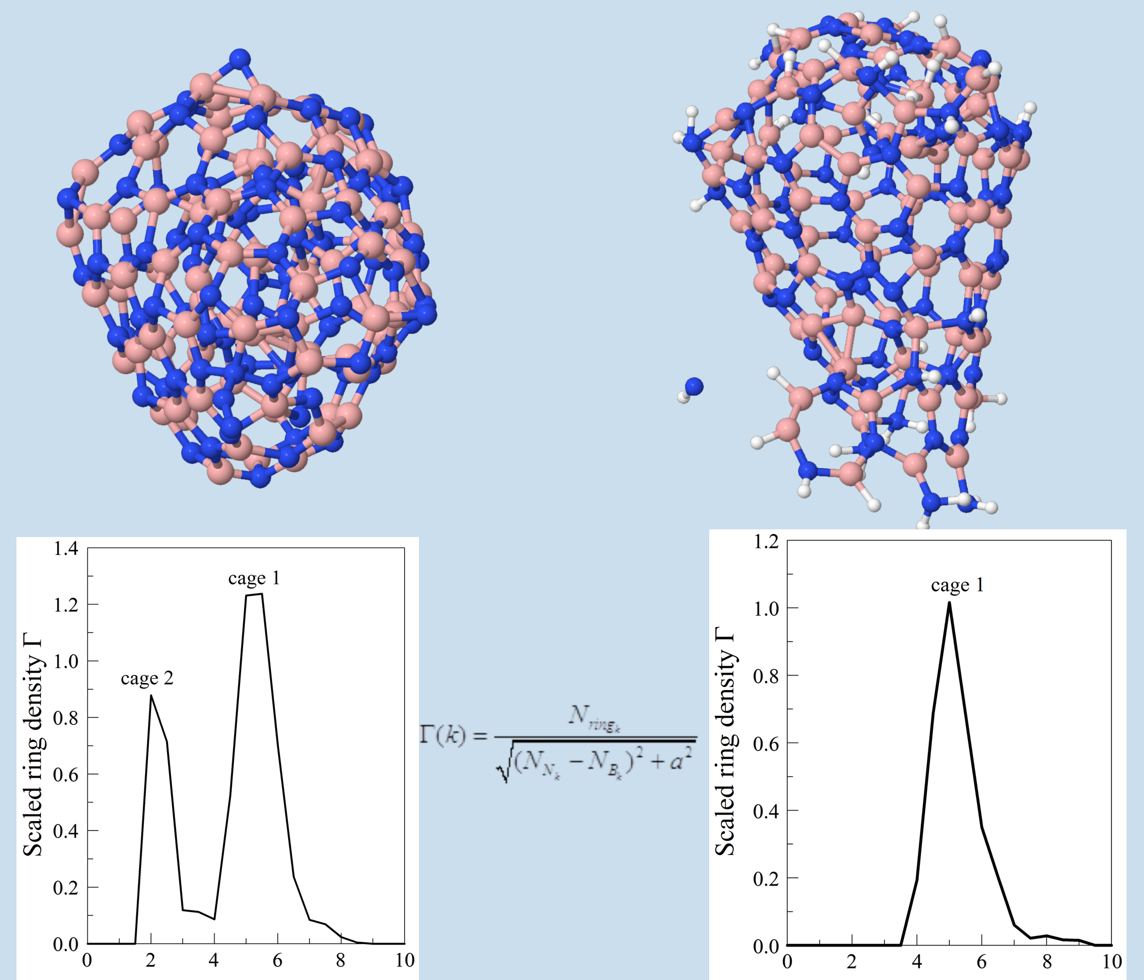


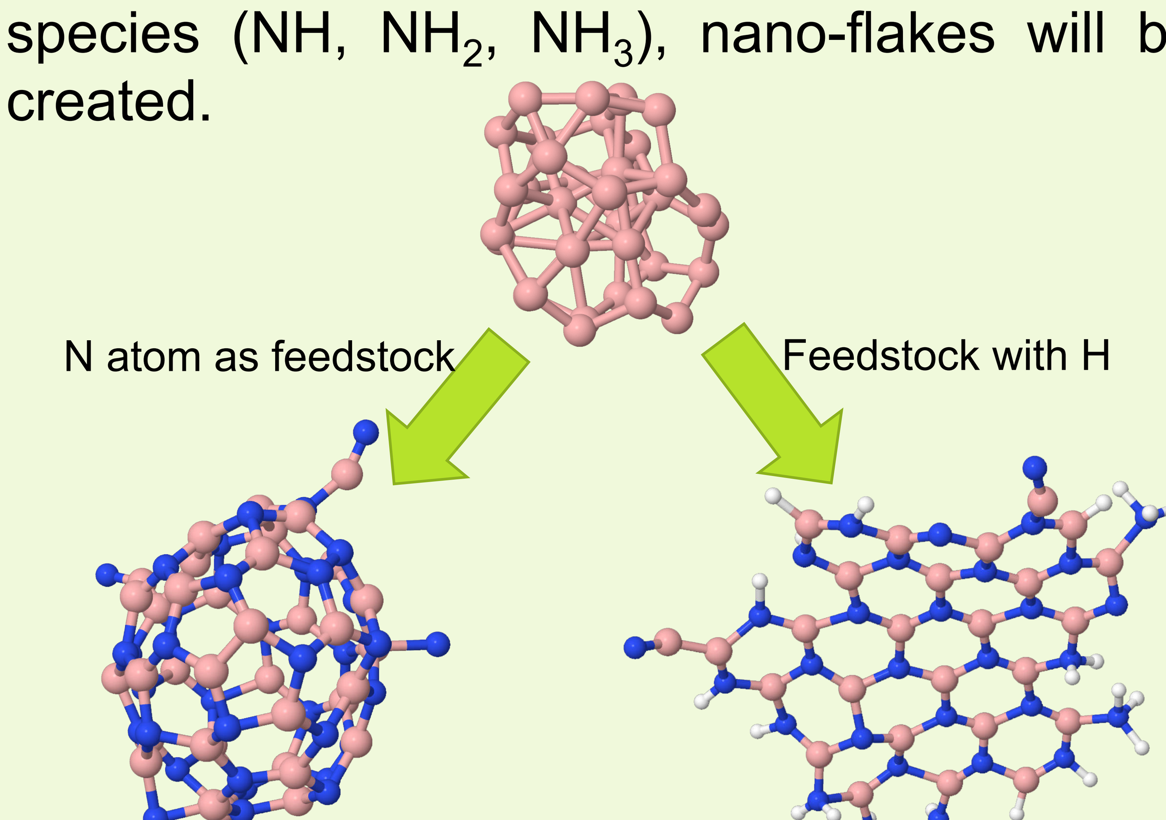
Figure 5. BN nanocages created by bombardment of N atoms (left) and NH molecules (right). Parameter Γ represents the valid BN hexagon density at different radius from the center of mass of the structure, and was plotted for the double-wall cage and single-wall cage, respectively.

Results above indicate the hydrogen effect at 2000K, at other temperature:

Temp	B96 + N	B96 + NH
1500K	dw BN cage	amorphous cluster
2500K	sw BN cage	sw BN cage (easily opens with continuous bombardment

Creation of BN nano-flakes

Small B clusters (B_{36}, B_{72}) can easily form single-wall BN cages when bombarded with N atoms. With bombardment of H containing species (NH, NH_2, NH_3), nano-flakes will be created.



Temperature dependence for the small B clusters is not significant:

- N atom feedstock: always single-wall cage
- Feedstock with H: always nano-flakes (for B_{72} the nanoflake is curved like a bowl)

Conclusions

We studied the hydrogen effect in the synthesis of BN nanostructures with quantum classical molecular dynamics approach:

- BN nano-diamonds (cBN) and nano-flakes can be created with N and H containing feedstocks, depending on the temperature and size of initial B cluster.
- With B clusters ~1nm in diameter (B_{96}), N creates double-wall (multiwall) cage structures. H with N suppresses the formation of DW nanocages, creating SW nanocages.
- BN nanostructures can transform from amorphous clusters (at 1500K) to cBN nanocrystals (at 2000K), and finally to BN nanocages (at 2500K).

References

1. Kim, Keun Su, et al. *ACS Nano* 8.6 (2014): 6211-6220.
2. Han, Longtao, and Predrag Krstić. *Nanotechnology* 28.7 (2017): 07LT01.
3. http://www.chemtube3d.com/solidstate/_blende(final).htm

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