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# Boron Nitride Nanotube Nucleation via Network Fusion during Catalytic Chemical Vapor Deposition

*Ben McLean,<sup>a</sup> Grant B. Webber,<sup>b</sup> Alister J. Page<sup>b\*</sup>*

<sup>a</sup> School of Environmental & Life Sciences, The University of Newcastle, Callaghan NSW  
2308 Australia

<sup>b</sup> Priority Research Centre for Advanced Particle Processing and Transport, The University of  
Newcastle, Callaghan NSW 2308 Australia

## **Abstract**

Despite boron nitride nanotubes (BNNTs) first being synthesized in the 1990s, their nucleation mechanism remains unknown. Here we report non-equilibrium molecular dynamics simulations showing how BNNT cap structures form during Ni-catalyzed chemical vapor deposition (CVD) of ammonia borane. BN hexagonal ring networks are produced following the catalytic evolution of  $H_2$  from the CVD feedstock, the formation and polymerization of B-N chain structures, and the repeated cleavage of homoelemental B-B / N-N bonds by the catalyst surface. Defect-free BNNT cap structures then form perpendicular to the catalyst surface via direct fusion of adjacent BN networks. This BNNT network fusion mechanism is a marked deviation from the established mechanism for carbon nanotube nucleation during CVD, and potentially explains why CVD-synthesized BNNTs are frequently observed having sharper tips and wider diameters, compared to CVD-synthesized carbon nanotubes.

## **Keywords**

Boron nitride, nanotube, chemical vapour deposition, nucleation, molecular dynamics

## 1. Introduction

Boron nitride (BN) is a chemical compound that has only recently been found in nature.<sup>1</sup> BN allotropes include zero-dimensional (0D) octahedral BN fullerenes (“fulborenes”),<sup>2</sup> 1D nanotubes (BNNTs),<sup>3</sup> nanowires,<sup>4</sup> nanofibers<sup>5</sup> and nanorods,<sup>6</sup> 2D h-BN as nanosheets,<sup>7</sup> nanomesh<sup>8</sup> and nanoribbons<sup>9</sup> and 3D analogues to diamond (c-BN and w-BN).<sup>10</sup> The two most studied BN nanomaterials are h-BN and BNNTs. Both are insulators<sup>11</sup> that exhibit remarkable thermal stability and mechanical strength, hence have attracted interest for a wide range of applications such as the reinforcement of polymeric films,<sup>12</sup> bioactive ceramics,<sup>13</sup> optoelectronics<sup>14-16</sup> and sensing applications.<sup>17-18</sup>

The most common method for h-BN and BNNT synthesis is catalytic chemical vapor deposition (CVD), which has been studied extensively experimentally (see reference<sup>19</sup> and references therein). A range of precursors (e.g. ammonia borane,<sup>20-25</sup> borazine,<sup>22, 26-29</sup> trichloroborazine,<sup>30</sup> diborane/ammonia,<sup>31</sup> trimethylamine borane<sup>32</sup>), catalysts (e.g. Ni(111),<sup>21, 26, 30</sup> polycrystalline Cu,<sup>22, 28, 33-35</sup> Pt,<sup>29</sup> Co,<sup>36</sup> Ru(0001),<sup>27</sup> and Rh(111)<sup>8</sup>) and experimental conditions have been investigated for the synthesis of h-BN and BNNTs.

Ammonia borane CVD holds particular importance since it produces monolayer h-BN<sup>37</sup> and has enabled a somewhat systematic approach to optimizing CVD conditions to achieve reproducible and high-quality BN structures.<sup>23-25</sup> For instance, low-temperature decomposition of ammonia borane is often performed prior to h-BN growth to afford more reactive, polymeric radical species and borazine.<sup>20, 37</sup> Grobert et al.<sup>38</sup> have recently shown that temperature-dependent ammonia borane decomposition can greatly influence h-BN morphology. Further, Suib et al.<sup>39</sup> demonstrated that pyrolytic decomposition of ammonia borane (> 1500 K) yields semi-crystalline h-BN. In recent years, theoretical approaches<sup>40-41</sup> have shed some light on how BN nanostructures form during high-temperature (<5000 K) pyrolysis of ammonia borane

(without a catalyst) and boron oxide CVD<sup>42</sup> via H<sub>2</sub> evolution and BN chain polymerization. Growth mechanisms of h-BN under CVD conditions have also been elucidated via experiment and theory, and it is now generally agreed that CVD growth of h-BN is surface mediated (see reference<sup>19</sup> and references therein). Yakobson et al.<sup>43</sup> proposed an atomic mechanism for the nucleation of h-BN islands on Ni(111) in agreement with prior experiments.<sup>23, 44-45</sup> Ding et al.<sup>46</sup> demonstrated that non-hexagonal rings are energetically unfavorable on Ni(111) and Edgar et al.<sup>47</sup> showed an elementary nucleation and growth process of h-BN on Ni(111) from elemental B and N. Recently, Edgar et al.<sup>48</sup> also showed that varying B:N feed ratios can tune the size and shape of h-BN lattices grown on Ni (111).

In contrast, our understanding of how BNNTs nucleate during catalytic CVD is relatively poor, despite it being almost 20 years since BNNTs were first synthesized via NiB-catalyzed CVD of ammonia borane.<sup>49</sup> Since Ni has been shown to be an effective catalyst for the CVD growth of BNNTs,<sup>50</sup> we focus on this catalyst metal here. Experiment has since shown that BNNT can proceed via either tip-<sup>51</sup> or root-growth modes, the latter more prevalent in cases of a metal catalyst.<sup>49-50</sup> Typically however, CVD-produced BNNTs exhibit wider diameter distributions (e.g. >> 10 nm) than CNTs, which can be routinely produced with narrow diameters (e.g. ~1 nm). Also, the morphology of BNNT tips is typically different from CNT tips; whereas CNT tips are dome-like, following Smalley's "yarmulke" cap formation mechanism,<sup>52</sup> BNNT tips often exhibit pronounced, sharp edges and corners. While theoretical approaches have focused on structural and energetic aspects of BNNT cap structures,<sup>53-56</sup> there remains no mechanistic description of how such BNNTs morphologies are formed during catalytic CVD.

In this work, we present nonequilibrium MD simulations that reveal the nucleation mechanism of BNNTs during Ni-catalyzed CVD of ammonia borane. BNNT nucleation is initiated via several stages, viz. (1) the Ni-catalyzed production of H<sub>2</sub> following B-H bond

activation, (2) the formation and oligomerization of surface-bound BN chains, (3) homoelemental (B-B, N-N) bond cleavage by the Ni catalyst to afford ring closure. Extended networks of BN hexagonal rings then form rapidly, yet remain free of 5|7 and 4|8 defect pairs, and are adsorbed perpendicular to the catalyst surface. Defect-free BNNT tip structures then form via direct fusion of adjacent BN networks via their zigzag edges. This mechanism is a marked departure from the established mechanism by which carbon nanotube (CNT) caps form, whereby the CNT cap structure remains strongly coordinated to the catalyst surface, forming small-diameter and round caps. The BNNT nucleation mechanism reported here is consistent with experimentally-observed BNNT tip structures, which are often flatter and sharper than those observed for CNTs, and have larger diameters.<sup>49</sup> The mechanism reported here offers key insight into the BNNT growth mechanism, and provides direct evidence that BNNT and CNT nucleation and growth are fundamentally different.

## 2. Methods

Non-equilibrium MD simulations were performed employing the ReaxFF method<sup>57</sup> as implemented in the SCM software package.<sup>58</sup> ReaxFF defines energy as a function of the bond order, based on the interatomic distance. All bond orders are calculated on-the-fly at each MD iteration. We use the ReaxFF force field, built from that previously shown to accurately describe ammonia borane decomposition<sup>40</sup>, H adsorption on Ni,<sup>59</sup> and Ni-catalyzed BN network formation,<sup>47</sup> for all simulations reported here. MD simulations were performed with an NPT ensemble enforced on the entire system via the Berendsen barostat.<sup>60</sup> The target pressure was maintained at 1 atm (damping constant 500 fs) throughout all simulations. The target temperature was held at either 1000 K, 1500 K or 2000 K (damping constant 100 fs). These target temperatures are centred on typical operating temperatures for CVD during the

growth of BN nanomaterials.<sup>20, 22, 25</sup> Newton's equations of motion were iterated using the velocity-Verlet algorithm<sup>61</sup> with a timestep of 0.25 fs, allowing the bond orders to vary continuously throughout the simulation. Each NPT-MD trajectory was first equilibrated with 10,000 non-reactive iterations prior to each reaction. Multiple unique trajectories were run for each simulation to ensure that a representative chemical mechanism was obtained. All quantitative data presented here is calculated as the mean of five trajectories. The ReaxFF potential employed here is validated in Figures S6-S9 via comparison against first-principles calculations density functional theory (DFT) adsorption energies of pertinent  $B_xN_yH_z$  adsorbates. These adsorption energies employed  $B_xN_yH_z$  fragments adsorbed on a  $4 \times 4 \times 5$  model Ni(111) slab. DFT calculations employed the Perdew–Burke–Ernzerhof (PBE)<sup>62</sup> generalized gradient approximation functional and the projector augmented wave (PAW) method. All DFT calculations were performed using the Vienna ab initio Simulation Package (VASP)<sup>63-64</sup> employing Gaussian smearing, an energy cutoff of 400 eV, energy convergence of  $1 \times 10^{-4}$  eV and G-centered  $1 \times 1 \times 1$  k-point mesh. The geometries of all structures were relaxed using a nuclear force threshold of 0.01 eV/Å.

We systematically evaluate the decomposition of ammonia borane as a function of temperature and the presence of either a  $B_{102}$  or  $Ni_{147}$  nanoparticle catalyst under typical CVD conditions. This is achieved by a set of eighteen distinct simulations, detailed in Table S1. Here we focus on the simulations held at 1500 K as this temperature represents the closest to those used in CVD experiments for the growth of h-BN.<sup>20, 22, 25</sup> All simulations employ periodic boundary conditions. The simulations in which two H atoms were manually removed every 10 ps after 1 ns of simulation are continuations of each trajectory up to that point. This probes the influence of the hydrogen chemical potential on the kinetics of BN nucleation. All H atoms removed across the simulations in this work were selected at random from those within a sphere of radius 4.5 Å from a boron atom. The removal of H atoms adopted in these simulations simply

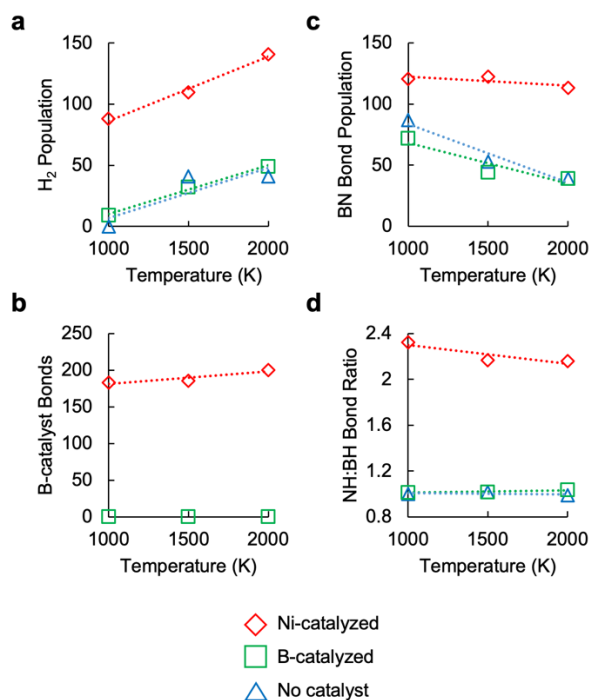
imitate and accelerate the natural H<sub>2</sub> formation mechanism (via B<sub>x</sub>N<sub>x</sub>H<sub>nx</sub> dissociation) observed across all trajectories. We note that similar approaches have previously been used to examine H removal during the formation of BNNTs,<sup>42</sup> CNTs,<sup>65-66</sup> fullerenes<sup>67</sup> and polyaromatic hydrocarbons.<sup>68</sup>

### **3. Results and Discussion**

#### **3.1. Ammonia Borane CVD Mechanism**

We investigate the mechanism of catalytic ammonia borane CVD as a function of catalytic activity, temperature and hydrogen chemical potential. Catalytic activity is measured by comparing Ni and B nanoparticle substrates against gas-phase pyrolysis (i.e. no catalyst at all). Boron is a relevant substrate for this comparison, since boron nanoparticles have been observed at the ends of BNNTs following CVD synthesis<sup>69</sup> and synthesis via laser heating,<sup>70</sup> and were presumed to have acted as catalysts. Full details of the conditions used in all simulations are presented in Table S1. Figure 1 summarizes the main aspects of ammonia borane CVD as a function of catalyst activity and temperature, viz. H<sub>2</sub> production (Figure 1(a)), precursor adsorption to the catalyst (Figure 1(b)), B-N bond formation (Figure 1(c)) and the N-H:B-H bond ratio (Figure 1(d)). Data in Figure 1 was obtained after 10 ns of simulation; all data during the first 10 ns are presented in Supporting Information (Figures S1-2).

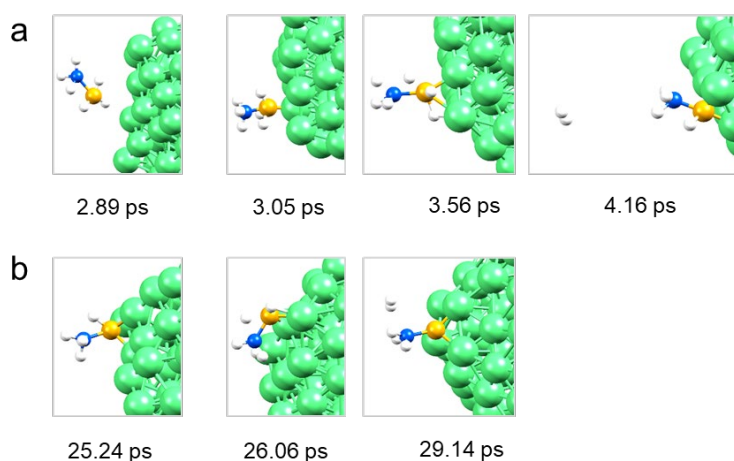




**Figure 1.** Summary of ammonia borane CVD as a function of catalyst activity and temperature. (a) H<sub>2</sub> production. (b) Precursor adsorption (measured via the number of B-catalyst bonds). (c) BN bond formation. (d) The ratio of NH to BN bonds. All data averaged across 5 trajectories after 10 ns of nonequilibrium MD simulation; complete data as a function of time is provided in Supporting Information.

It is immediate from Figure 1(a) and (b) that Ni-catalyzed ammonia borane CVD is characterized by rapid production of H<sub>2</sub> and precursor adsorption to the Ni catalyst via the formation of Ni-B bonds. The catalytic activity of Ni is far greater than that of the B nanoparticle in this respect, as anticipated. At these temperatures, the Ni catalyst is most likely molten and hence not crystalline; Lindemann indices ranged between  $\sim 0.15$  at 1000 K to  $\sim 0.23$  at 1500 and 2000 K, indicating that the surface is molten throughout the CVD and nucleation processes. This is consistent with prior investigations of Ni nanoparticle melting based on QM/MD simulations.<sup>71-72</sup> The Ni nanoparticle surface becomes B-saturated within 1 ns of simulation time irrespective of the temperature. Figure 1(b) shows a greater number of Ni-B bonds than there are atoms in the nanoparticle itself, independent of temperature, since each surface-adsorbed B is coordinated on average by  $\sim 4$  Ni atoms. Dissolution of B atoms into the nanoparticle subsurface/bulk is not observed on the timescales considered here, and remain

adsorbed to the outer surface. In contrast, during Ni-catalyzed CNT growth C atoms readily dissolve into the Ni catalyst and precipitate onto the Ni surface before participating in nucleation and tube growth.<sup>73-74</sup> The rapid kinetics of Ni-B bond formation here are consistent with the presence of stable NiB phases observed in several BNNT CVD growth experiments.<sup>49</sup> It is conceivable that the surface saturation of the Ni nanoparticle observed here is the first step in the formation of such boride phases, which will occur over much longer timescales than those used here. By contrast, essentially no B-B bonds are formed between ammonia borane precursor species and the B nanoparticle. This indicates inelastic collision of precursor molecules with the B nanoparticle dominates instead of catalytic adsorption. Similar results are observed during simulations of boron oxide CVD.<sup>42</sup> Unsurprisingly therefore, the rate of H<sub>2</sub> production in the presence of a B nanoparticle also does not significantly exceed that observed from gas-phase pyrolysis of ammonia borane at the same temperature (Figure 1 (a)), nor does the rate of B-N bond formation (Figure 1 (c)).



**Figure 2.** (a) Ni-catalyzed production of H<sub>2</sub> from ammonia borane, producing NH<sub>3</sub>BH bonded to the surface via a Ni-B bond. (b) Ni-catalyzed production of H<sub>2</sub> from surface adsorbed NH<sub>3</sub>BH. H is abstracted from another surface group followed by H transfer from B to N and release of H<sub>2</sub> to afford NH<sub>3</sub>B. Green, blue, orange, and white spheres represent Ni, N, B and H atoms, respectively. Images are taken from the Ni-catalyzed simulation at 1500 K.

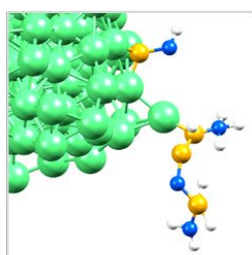
The fact that the Ni catalyst surface becomes boron-saturated suggests that boron has a stronger affinity for the surface, compared to Ni. In the absence of hydrogen, Yakobson et al.<sup>75</sup> have shown this to be the case for pristine h-BN edges, with ReaxFF contradicting results obtained using density functional theory (DFT). However, Figures S6-S9 show that the ReaxFF potential employed here is generally in good agreement with DFT adsorption energy calculations of pertinent  $B_xN_yH_z$  fragments adsorbed to a Ni(111) surface. In the case of the ammonia borane precursor, the tendency for surface saturation with boron arises from the relative rates of B-H and N-H bond cleavage at the Ni catalyst surface. Surface saturation of the Ni catalyst with boron is coupled with the release of H<sub>2</sub> from the ammonia borane precursor via the mechanism depicted in Figure 2(a). Adsorption of ammonia borane on the Ni surface is immediately followed by selective B-H bond activation/cleavage, intramolecular hydrogen transfer and finally the release of H<sub>2</sub> from the -NH<sub>4</sub> intermediate moiety. Ultimately H<sub>2</sub> is released within ~2 ps of the ammonia borane precursor adsorbing to the catalyst surface. While this mechanism is temperature-independent, the total H<sub>2</sub> production increases with temperature, indicating that it is kinetically limited. The Ni catalyst facilitates further H<sub>2</sub> evolution from the H<sub>3</sub>N-BH species produced in Figure 2(a) until all B-H bonds in the adsorbed precursor are consumed via the same B-H bond activation / intramolecular H transfer mechanism, as shown in Figure 2(b). Figure 1(d) shows this selective activation of B-H bonds is a general feature of the Ni-catalyzed ammonia borane CVD process; between 1000-2000 K there are consistently ~2 – 2.5 times more N-H bonds than B-H bonds. This means B atoms have a greater opportunity to chemisorb to the surface via passivation of their dangling bonds, which leads to surface saturation. By contrast, the number of N-H and B-H bonds with a B nanoparticle and in gas-phase are equivalent across this temperature range.

Although the B nanoparticle infrequently abstracts H from ammonia borane (see Figure S3), it does not appreciably influence the nucleation of any BN structures. By comparison, the Ni

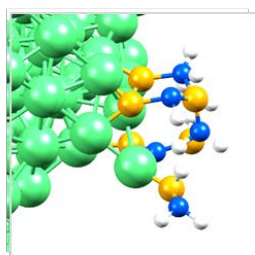
catalyst accelerates B-N bond formation by an approximate factor of two (despite B-N bonds initially decreasing due to thermal activation of gas-phase ammonia borane molecules, see Figure S2). Fewer B-N bonds are observed at higher temperatures due to increased thermal activation of B-N bonds, irrespective of the catalytic substrate present. Interestingly, however, this trend is mitigated by the Ni catalyst, for which the decrease in B-N bonds is far smaller than that observed with a B nanoparticle and in gas-phase (which are equivalent). The reasons for this are twofold. Firstly, the Ni catalyst stabilizes growing BN fragments on its surface via strong Ni-B bonds, making them more thermally stable. Secondly, the BN networks formed in the presence of Ni are larger, and therefore more resistant to thermal activation.

Thus, Ni-catalyzed BNNT growth is ultimately driven by the high boron chemical potential at the catalyst surface, due to B atoms being liberated from the precursor via selective B-H bond activation, and strong Ni-B bonds stabilizing B atoms on the catalyst surface. The high boron chemical potential enables rapid formation of B-N bonds with nearby  $\text{NH}_x$  groups adsorbed/adsorbing to the catalyst surface, which are necessary for the nucleation of BN rings, the building blocks of BNNTs.

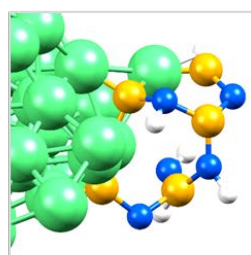
a



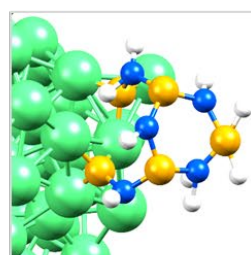
13 ps



419 ps

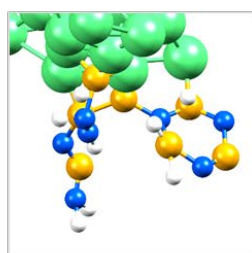


534 ps

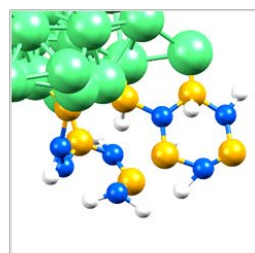


700 ps

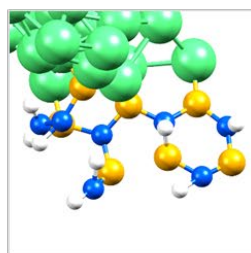
b



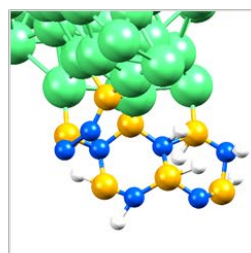
1.462 ns



1.470 ns

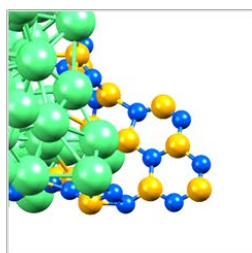


1.475 ns

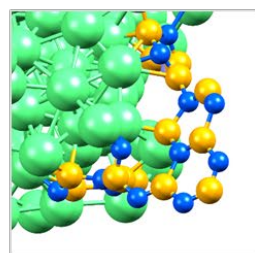


1.482 ns

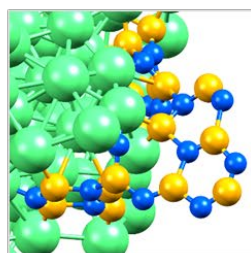
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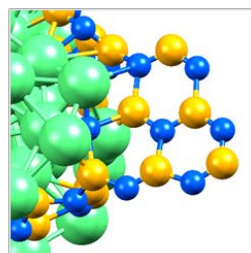
2.92 ns



2.93 ns

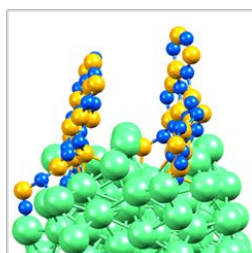


2.95 ns

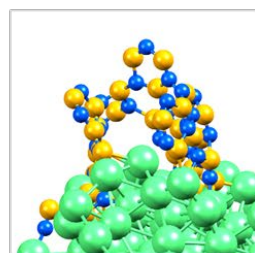


3.00 ns

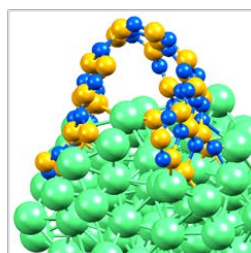
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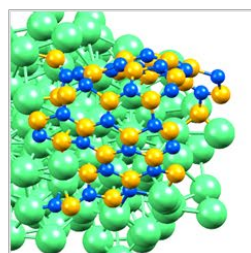
17.714 ns



17.717 ns

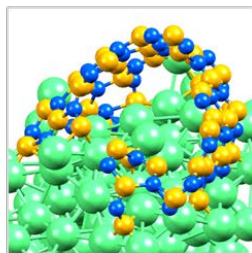


17.720 ns

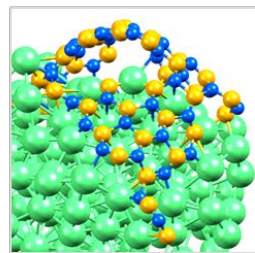


17.720 ns

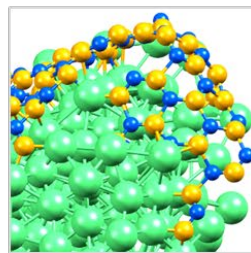
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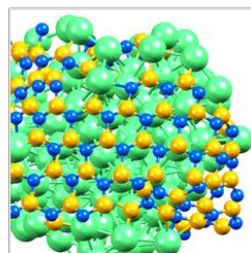
20 ns



25 ns



30 ns



30 ns

**Figure 3.** (a) Surface-bound BN chain oligomerizes with adjacent surface group and forms new B-N bonds. Ni catalyst facilitates B-B bond cleavage in surface-bound chain and allows B-N bond to form to nucleate the first ring in the BNNT tip structure. (b) Surface-bound BN chain linked to first ring via B-B bond. Ni catalyst facilitates B-B bond cleavage to allow nucleation of second BN ring. (c) Ni-catalyzed N-N bond cleavage in a surface-adsorbed B-N chain followed by B-N bond formation with the surface-bound N atom, closing the third ring in the BN network. (d) Two separate BN ring networks stabilized perpendicular to the Ni catalyst surface via strong Ni-B bonding. Rapid B-N bond formation takes place as soon as the two networks are close enough in proximity, resulting in the two networks fusing to form a BNNT tip, akin to a CNT cap. Two images are shown of the BNNT tip structure at 17.720 ns, from the side and from the top. (e) BNNT tip evolution over a further 13 ns of simulation time. Nearby surface species diffuse on the Ni catalyst and add to the BNNT tip, increasing coverage of the Ni nanoparticle. The BNNT tip rounds slightly after 30 ns but remains entirely free of topological defect rings. Two images are shown of the BNNT tip structure at 30 ns, from the side and from the top. Atom colors as in Figure 2. Images are taken from the Ni-catalyzed simulation at 1500 K.

### 3.2. BNNT Nucleation Mechanism

BN ring formation is only observed in the presence of a Ni catalyst and occurs via the mechanism shown in Figure 3. The nucleation process begins with the Ni-catalyzed production of H<sub>2</sub>, which facilitates BN chain growth from the surface (Figure 3 (a), 13 ps). Typically, such chains are partially saturated, meaning they are only tethered to the surface via a single Ni-B bond. Thermal energy therefore drives oligomerization with other surface-adsorbed BN groups via B-N bond formation (Figure 3 (a), 419 ps). Notably, chains thus formed may contain homoelemental bonds (predominantly B-B bonds), which are energetically unfavorable<sup>53-56</sup> in BN rings and BNNTs. We observe such “defects” to be removed quickly to form BN structures composed exclusively of B-N bonds.<sup>41-42, 47</sup> Figure 3 (a) (534 ps) shows the Ni catalyst facilitating this healing process, via B-B bond cleavage and subsequent B-N bond formation with adjacent surface-adsorbed BN groups. The mechanism shown in Figure 3 was never observed when surface-adsorbed BN chains were fully hydrogen saturated. Hence, H<sub>2</sub> production is essential for the nucleation of BN rings in ammonia borane CVD. As detailed

above this crucial aspect of the CVD process is facilitated by the Ni catalyst, but not by the inactive B nanoparticle or gas-phase pyrolysis of ammonia borane. An active catalytic surface is therefore critical for BNNT nucleation and growth during CVD.

Following the initial nucleation of the BN hexagon shown in Figure 3(a), an extended BN hexagon network forms via repeated Ni-catalyzed activation and cleavage of B-B and/or N-N bonds in the growing fragment, combined with H<sub>2</sub> elimination, as shown in Figure 3(b) and 3(c). The growth of the BN ring network proceeds from the base of the structure as BN chains grow and diffuse on the surface. The activation and cleavage of N-N bonds by the Ni catalyst is notable, but not unexpected, as the N-N bonds observed at the Ni surface are primarily N-N single bonds (not N≡N triple bonds which require 225.8 kcal mol<sup>-1</sup> to be broken<sup>76</sup>). The fact that such cleavage is not observed in gas-phase or on the B nanoparticle highlights another important role the Ni catalyst plays during BNNT CVD synthesis, i.e. activation of homoelemental bonds in the growing BNNT structure. N<sub>2</sub> itself is actually evolved from the catalyst surface in relatively small amounts (Figure S1). H<sub>2</sub> elimination reduces hydrogen passivation of B- and N- dangling bonds, and thereby promotes the association of neighboring surface groups. Hence, in the presence of a reduced H<sub>2</sub> chemical potential, we observe the linking of BN rings on the Ni surface and the condensation of extended BN hexagonal ring networks. We return to a more complete discussion of the influence of the H<sub>2</sub> chemical potential in the next section.

The condensation of BN rings shown in Figure 3(c) occurs while the ring stands perpendicular to the Ni surface, while it is adsorbed via only a few Ni-B and Ni-N bonds. BN ring networks are not observed to condense and grow while fully coordinated to the surface, as observed for h-BN,<sup>21, 43, 47-48</sup> and indeed CNTs<sup>52, 77</sup> and graphene as well.<sup>78-79</sup> This is attributed to both the effect of hydrogen, which passivates dangling B- and N- bonds (preventing the network from fully adsorbing to the surface), and the high positive curvature of the Ni

nanoparticle surface. A pervading assumption in the literature is that BNNTs nucleate on metal catalysts via a mechanism similar to that for CNTs, i.e. via a “cap” structure reminiscent of a yarmulke, leading to round-ended CNTs.<sup>52</sup> However, the structure of BNNT tips is far less documented and studied experimentally, compared to CNT caps. BNNT diameter distributions are typically larger than CNT diameter distributions, which suggests that BN networks are incapable of forming via small cap structures required for a narrow diameter tube (i.e. due to high curvature and hence strain). Notably, BNNTs exhibiting flat tip structures with “sharp” corners, inconsistent with a CNT-like yarmulke cap structure (which is dome-like), have been frequently observed and reported via TEM,<sup>49, 80-81</sup> Such BNNT tip morphologies have been attributed to the incorporation of BN moieties at the junctions between the growing BNNT and the catalyst surface,<sup>49</sup> the incorporation of 4-membered rings occupying the corners of the tube end,<sup>80-81</sup> and pentagons present at the end of the BNNT tip.<sup>49, 80-81</sup>

Results presented here provide an alternate explanation of the origin of BNNT tip structures. Figure 3(d) shows that distinct BN ring networks that have grown perpendicular from the catalyst surface ultimately fuse via the rapid formation of B-N bonds between adjacent rings at the zigzag edges of both networks. Once formed, the junction between these two individual BN networks consist of hexagonal rings, and do not include defects such as 4-membered rings or pentagons. The typically larger BNNT diameters observed via CVD growth using Ni catalysts is a natural consequence of this fusion nucleation mechanism. For instance, a BNNT will only grow after its tip is fully formed on the catalyst surface, and results in Figure 3 indicate that this first requires the formation of distinct BN networks on the catalyst surface. Figure 3(e) shows the evolution of the BNNT tip up to 30 ns of simulation. Here the tip structure now covers a significant portion of the Ni nanoparticle surface and has rounded and flattened slightly. Still, we note that the tip entirely consists of BN hexagons and no pentagons or any other defects are observed within its structure. Presumably this is due to the effect of the

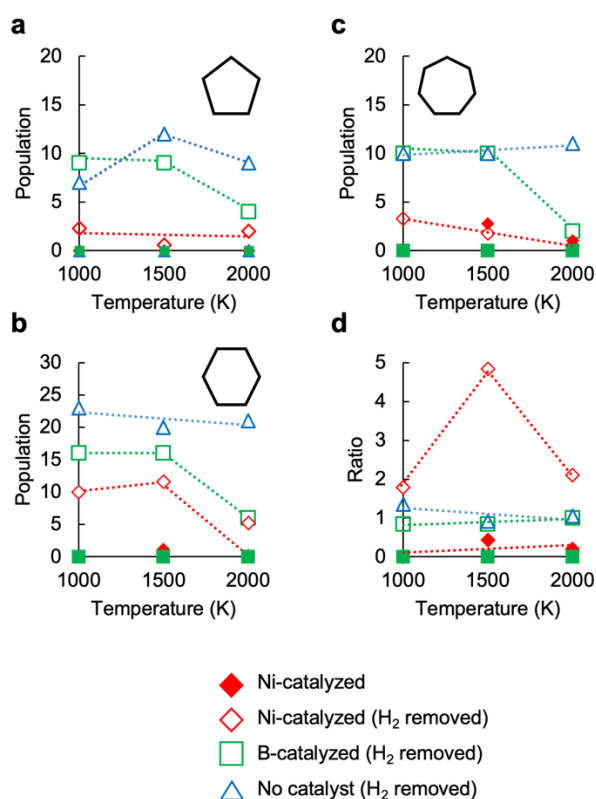


catalyst nanoparticle, which enables the hexagon-only structure to adopt a positively curved structure (matching that of the nanoparticle) without forming structural defects. This is potentially assisted by the relatively large diameter of the tip structure itself, since this curvature does not yield excessive strain. On the basis of experimental observations<sup>80-81</sup> it has been hypothesised that the observed shapes of BNNT caps are perhaps due to topological defects, such as pentagons or squares. While the stable cap structures we observe here do not feature such topological defects, they do not preclude them from occurring. We note that, in absence of a 2<sup>nd</sup> network, single BN networks are incapable of forming BNNT tips (e.g. Figure S5). Considering the rapid rate with which such BN networks form, and the fact that they do not diffuse across to the surface (due to their strong terminating Ni-B and Ni-N bonds) but are adsorbed perpendicular to it, the individual networks can be expected to be large prior to fusion, and hence the tip structures that are formed from them are likely to be significant in diameter, even before BNNT growth takes place. This is consistent with the relative diameters of the BNNT tip and Ni catalyst shown in Figure 3(d) (1.12 and 1.36 nm, respectively), which are comparable. By contrast, a CNT cap structure only requires 6 pentagons before CNT growth occurs with a fixed diameter,<sup>82</sup> meaning that relatively small caps and narrow diameters are possible during CNT growth. Whether or not the diameter of the BNNT tip is limited by the diameter of the Ni nanoparticle catalyst remains the subject of ongoing research.

### **3.3. Influence of the Hydrogen Chemical Potential**

To elucidate the effect of the hydrogen chemical potential on BNNT nucleation, the natural B-H bond activation / H<sub>2</sub> formation mechanism detailed above has been simulated via the manual, random removal of two H atoms from the reaction at regular intervals of 10 ps; this frequency is comparable to the average frequency of H<sub>2</sub> production shown in Figure 2 (e.g. ~2 ps). As anticipated, decreasing the hydrogen chemical potential increases the number of B-N

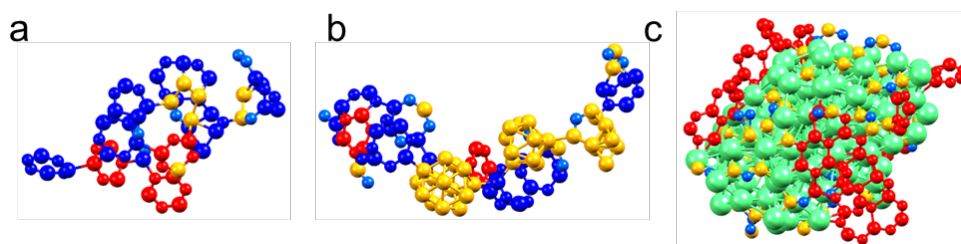
bonds on the Ni catalyst surface (Figure S2), and hence BN rings. Equivalent trends are observed in the gas-phase pyrolysis of ammonia borane and in the presence of the B nanoparticle, indicating that this is simply due to Le Chatelier – like behaviour (considering the chemical equation  $\text{H}_3\text{N}-\text{BH}_3(\text{g}) \rightarrow \text{BN}_{(\text{s})} + 3\text{H}_2(\text{g})$ ). Figure 4 compares populations of 5-, 6- and 7-membered BN rings as a function of the  $\text{H}_2$  chemical potential. While 4|8 ring pairs have been shown to be important structural components in BN nanostructures such as fulborenes,<sup>83</sup> and flat BNNT caps<sup>80-81</sup> we do not observe them in our simulations and so they are not considered in Figure 4.



**Figure 4.** (a) Population of BN pentagons after 10 ns. (b) Population of BN hexagons after 10 ns. (c) Population of BN heptagons after 10 ns. (d) The ratio of hexagons present to the sum of pentagons and heptagons after 10 ns. See Figure S4 for populations as a function of time.

Figure 4(a-c) shows the populations of BN *pentagons*, hexagons and heptagons, respectively, observed as a function of the catalyst activity and hydrogen chemical potential.

The number of pentagons and heptagons formed during gas-phase pyrolysis of ammonia borane are approximately equal, because they are formed in pairs. This is also observed at grain boundaries of h-BN<sup>84</sup> and in prior simulation studies with atomic BN precursors.<sup>47</sup> The number of hexagons is roughly double that of both pentagons or heptagons in this case, as they are energetically preferred. Nevertheless, BN networks formed during gas-phase pyrolysis are highly defective, as shown in Figure 5(a). Similar trends are observed in the presence of the B nanoparticle, i.e. formation of defect pentagons and heptagons in the nucleating BN network leads to highly defective BN structures. We note also that the B nanoparticle is unstable at 1500 and 2000 K in the presence of a reduced hydrogen chemical potential. At these temperatures, the B nanoparticle dissociates into smaller B<sub>12</sub> octahedral subunits that exhibit the capacity to anchor small BN networks during growth. Nevertheless, hydrogen abstraction from the ammonia borane precursor evidently stabilizes the B nanoparticle surface via passivation.



**Figure 5.** (a) Amorphous BN network formed after 10 ns at 1500 K via gas-phase pyrolysis of ammonia borane. (b) Defective BN network formed after 10 ns at 1500 K and removal of H<sub>2</sub> in the presence of a B substrate. The B catalyst substrate partially dissociates resulting in small B nanoparticles acting as anchor points for the growth of the BN network. (c) Defect-free BN networks formed after 10 ns in the presence of a Ni catalyst with a reduced hydrogen chemical potential. Red atoms are in hexagons, blue atoms are those in defective rings (i.e. non-hexagonal rings or rings containing homoelemental B-B / N-N bonds).

By contrast, the formation of defect rings with the Ni catalyst present is effectively suppressed. This leads to the growth of essentially defect-free BN networks, as indicated by the hexagon: defect ring ratio shown in Figure 4(d). CVD at 1500 K is evidently the “sweet

spot” for hexagon formation using a Ni catalyst; the number of hexagons produced at higher temperatures here drops, as expected, due to thermal activation of B-N bonds, and yields more amorphous/defective BN networks growing at the catalyst surface. We note that the Ni catalyst used here is stable at 2000 K, at least over the timescales we investigate here (e.g. >10 ns). While previous simulations of BN nanostructure growth under plasma conditions have shown the formation of BNNTs to be possible without a catalyst,<sup>41</sup> our results demonstrate that under CVD conditions, the nucleation of BNNTs is necessarily surface-mediated. This is in agreement with what has been shown for ammonia borane growth of h-BN structures.<sup>19</sup> Specifically however, the type of surface matters; while B nanoparticles are observed ex situ following catalytic CVD growth of BNNTs,<sup>49</sup> we have shown that the key moments in the nucleation mechanism are all facilitated via a Ni catalyst surface, as is the promotion of hexagonal BN rings and suppression of defect formation during nucleation.

#### **4. Conclusions**

We have reported the mechanism of BNNT nucleation on Ni catalyst nanoparticles during ammonia borane CVD, based on non-equilibrium molecular dynamics simulations. These simulations demonstrate the key catalytic role of Ni in the formation of BNNTs. BNNT nucleation occurs via several stages, viz. the Ni-catalyzed production of H<sub>2</sub> following B-H bond activation, the oligomerization of surface-bound BN chains, the facilitation of homoelemental (B-B, N-N) bond cleavage by the Ni catalyst to afford ring closure, and finally the growth of BN ring networks perpendicular to the catalyst surface. The formation of a BNNT tip structure then occurs via the direct fusion of adjacent BN sheet zigzag edges. This process differs significantly from the formation of CNT caps, which nucleate while fully coordinated to the catalyst surface, and produce rounded caps that can have relatively small diameters.

However, the kinetics of BNNT tip formation and CNT cap formation bear some resemblance to each other. It is widely agreed that, while CNT caps can form rapidly (e.g. on nanosecond timescales), the time required for CNT cap “lift-off” from the surface, whereby the cap is elongated into a tube, can take orders of magnitude longer (e.g. seconds). Indeed, the nature of this transition to continued growth, and the size of the critical nucleus that triggers it, largely remains an open question. Whether or not BNNT growth proceeds via an equivalent transition following the rapid formation of the BNNT tip also remains unclear.

Our mechanism of BNNT tip nucleation is consistent with experimentally-observed BNNT tip structures, which are often flatter and sharper, and associated with wider-diameter BNNTs.<sup>49</sup> Previously, BNNT tip formation was assumed to include the presence of 4|8 BN pairs or unstable pentagons at tip corners,<sup>80-81</sup> neither of which are observed here. BNNT nucleation via this mechanism requires a decreased hydrogen chemical potential, as hydrogen passivation hindered the condensation of large BN ring networks. The influence of temperature on this mechanism was also investigated; defect-free BN ring networks were observed at 1500 K, while at 1000 K, there was less Ni-catalyzed H<sub>2</sub> production and at 2000 K defective ring networks formed due to increased thermal activation of B-N bonds. In the presence of a B nanoparticle catalyst and in the absence of a catalyst, no BNNT tips were formed, and subsequent to hydrogen chemical potential decreasing, the BN networks that formed were highly defective. We believe the results reported here offer key insights into the BNNT growth mechanism, and direct evidence that BNNTs nucleate and grow during CVD in significantly different ways, compared to CNTs.

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### Supporting Information Available

Full details of all non-equilibrium MD simulation conditions, time-dependent populations of key reactive intermediates during ammoniac borane CVD, time-dependent bond populations during ammonia borane CVD, mechanism of H-abstraction from ammonia borane via a boron nanoparticle, time-dependent populations of BN polygonal rings, BN ring networks grown perpendicular to the Ni nanoparticle on opposite sides. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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## TOC Graphic

