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Letter

A path for synthesis of boron-nitride nanostructures in volume of arc plasma

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Abstract

We find a possible channel for direct nanosynthesis of boron-nitride (BN) nanostructures, including growth of BN nanotubes from a mixture of BN diatomic molecules by quantum–classical molecular dynamics simulations. No catalyst or boron nanoparticle is needed for this synthesis, however the conditions for the synthesis of each of the nanostructures, such as temperature and flux of the BN feedstock are identified and are compatible with the conditions in an electric arc at high pressure. We also find that BN nanostructures can be synthetized by feeding a boron nanoparticle by BN diatomic molecules, however if hydrogen rich molecules like NH_3 or HBNH are used as a feedstock, two-dimensional nanoflake stable structures are formed.

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(Some figures may appear in colour only in the online journal)

1. Introduction

Boron-nitride (BN) nanostructures (BNNSs) can be synthetized in various forms like fullerenes, nanocages, nanococoons, nanoflakes and nanotubes, similarly to the carbon nanostructures. Synthesis of BN nanotubes (BNNTs) is carried out experimentally by a number of methods, like arc discharge [1], laser ablation [2], substitution reactions from CNTs [3], ball-milling [4], chemical vapor deposition [5–7]. The ultimate goals of all methods are high-rate production of impurity and defect free nanostructures. Single-walled BNNTs (SWBNNTs), have chirality assigned similarly to single-walled carbon nanotubes (SWCNTs), exhibiting extraordinary mechanical and electronic properties. For example, the band gap of a BNNT of large radius is large (~5 eV) and rather insensitive to the tube structural features (such as chirality, and even multi-walled structure). However, Xiang *et al* [8] found that the band gap of small zigzag BN nanotubes ($R < \sim 4$) decreases rapidly with a decrease of the radius. Also, unlike CNTs, BNNTs have high oxidation resistance and extraordinary piezoelectric, electrostrictive, thermal, field-emission and optical properties. These properties make BNNTs very attractive for applications in robotics, for room-temperature hydrogen storage, for neutron and ultraviolet shielding composites, for enhanced cooling of electronic components, in biomedical applications, as a new composite in jet engines and for high performance batteries.

Complete understanding of the BNNT nanosynthesis process at the atomic level has been missing so far, mainly due to the heterogeneous nature of BNNSs. Most of the models invoke self-assembly processes through interaction of atomic nitrogen [9–18] or a compound containing nitrogen [19] with the boron nanodroplets. This resembles to the root-growth mechanism of the SWCNT synthesis from a nanometer-sized transition metal catalyst, as described by Lee *et al* [2], and Arenal *et al* [10]. According to this model a nanocage grows by adding the feedstock N atoms into a small amorphous B cluster, to form sp^2 BN caps of hexagons on the surface of the B particle. The cap structure is then transformed into a hollow tube structure by the growth of an sp^2 h-BN sheet around the rim of the cap.

The pioneers in experimental studies of the BN fullerenes were Stephan *et al* [9], and Goldberg *et al* [11], who published their observations almost two decades ago. Over ten years ago, Oku *et al* [12, 13] confirmed the existence of several classes of BN fullerenes, using arc melting technique and mass spectroscopy. The high-temperature plasma process (5000–20 000 K) has also demonstrated great potential in the BNNT synthesis [14]. Kim *et al* [19] reported a high-yield production of BNNT by feeding hexagonal boron nitride (h-BN) powder along with hydrogen and nitrogen gases which dissociate into atomic constituents in a high temperature plasma (>8000 K) at atmospheric pressure. The model for BNNT synthesis that Kim proposes upon his experiment assumes creation of nanodroplets of boron, and association of B, N, and H atoms into H_xBNH_x. These H-containing species dissociate at the boron droplet surface into BN radicals, supplying a rapid BNNT growth. Role of hydrogen is seen in stabilization of N feed, impeding a recombination of N radicals. Zettl *et al* [15] have used plasma torch in nitrogen atmosphere at high pressure (a few atms) with boron feedstock to produce BNNTs, as well as BN nanococoons and h-BN-flake nanostructures. At pressures above 3 atm a production of BNNTs was dominant, whereas the other BN nanostructures were dominantly synthetized at lower pressures. The authors interpreted their results by the root-growth mechanism, assuming that boron nanoparticles become molten droplets in the plasma plume. While in the plume, the droplets react with nitrogen atoms created by the dissociation of N_2. Higher pressure rises the energy density and the collision rate of N atoms with the boron droplets, stimulating BNNT growth.

The mechanism by which N atoms are incorporated into the B compounds to form alternant BN bond superstructures, which develops under high temperature conditions, has not been analyzed at all until recent theoretical work of Ohta [16], inspired by the experiments of Oku *et al* [17, 18]. Ohta applied quantum–classical molecular dynamics (QCMDs), to successfully build BN nanocages bombarding a small boron cluster, B_{36}, with nitrogen atoms each 4 ps, and treating the whole system as a canonical (NVT) ensemble at temperature of 2000 K. After 50 hits of N, the whole system self-organized into a nanocage, with dominant hexagon structure, using all boron atoms for BN bonds. Excess of nitrogen atoms was either reflected or emitted in form of N_2. Thus, the cage size was predetermined by the size of the initial boron cluster. However, Ohta's simulations were not successful in growing a BNNT.

Difficulty in obtaining atomic nitrogen by dissociation of N_2 is the main reason for not having a direct connection of these models with the relevant experiments. In this regard, it is very interesting to note the work of Blase *et al* [20] who showed, using classical molecular dynamics (CMDs) simulations, that different growth mechanisms can be associated with different chiralities and that armchair SWBNNT can develop an ordered metastable edge, i.e. it can grow un-catalyzed. This is connected to energetically favoring polygons with alternate B–N bonding at the tip of the growing tube. Thus, the B–N bond (~4.0 eV) is energetically favorable in comparison to the B–B (~3.1 eV) and a single-bond N–N (~1.7 eV) in the BN nanostructures, which also leads to the conclusion that even-numbered rings, composed of the B and N alternations are dominating, preventing formation of B–B and N–N bonds [21]. Still, energetically unfavorable odd-numbered rings could appear in the nanocages, as a form of defects [22].

In this report, we show that various BN nanostructures including BNNT growth can be built by self-organization from a mixture of BN diatomic molecules, without a boron cluster assisted root-growth mechanism. This synthesis evolves at high temperatures and concentrations, consistent with the conditions in the volume of an electric arc plasma at high pressure. We also show that nanoflakes can be built at high temperatures by interaction of hydrogen-rich molecules, NH_3 and HBNH, with the boron droplet. Although we use the QCMD method similar to Ohta's [16], explained in more details in section 2, our results are independent on a supply of atomic hydrogen and are in marked difference with the commonly accepted BNNS formation theories based on the root-growth mechanism. Our results and their analysis are shown in section 3, while section 4 contains our conclusions.

2. Model and methods

Our simulations of BNNSs were performed by using QCMD with approximation to DFT for the quantum component of simulation, i.e. using the self-consistent charge (SCC)-DFTB simulations [23–25]. Like Ohta [16], we have also shown that, surprisingly, use of the SCC component of the tight-binding DFT (DFTB) approximation influences the synthesis too weakly to prevent the use of the faster computational benefit obtained when not using SCC in DFTB. We were able to fully reproduce Ohta's simulations. In addition we have also tried to use CMDs with various REAXFF potentials [26, 27] to simulate growth of BNNS, either by root-growth mechanism as in Ohta's work, or by direct synthesis of BN diatomic molecules. The REAXFF potentials include a possible role of coordinate-dependent charges in the dynamics, that would emerge from the higher electronegativity of N (3.04) in comparison to B (2.04). However, creation rate of BN polygons, and especially hexagons, as building elements of BNNS was very low even for extended time of 10 ns, without any indication of the closure of the structures.

Consequently, these computational experiments show the use of quantum mechanics, even in its approximate form, is essential for successful simulations of the BNNS, while the role of charge exchange is not essential in the process. We have applied QCMD to find possible and optimal reaction pathways for the synthesis of BNNTs, BN nanocages (and fullerenes) and BN 2D flat nanostructures, under conditions of arc discharge (high temperature, high pressure). The

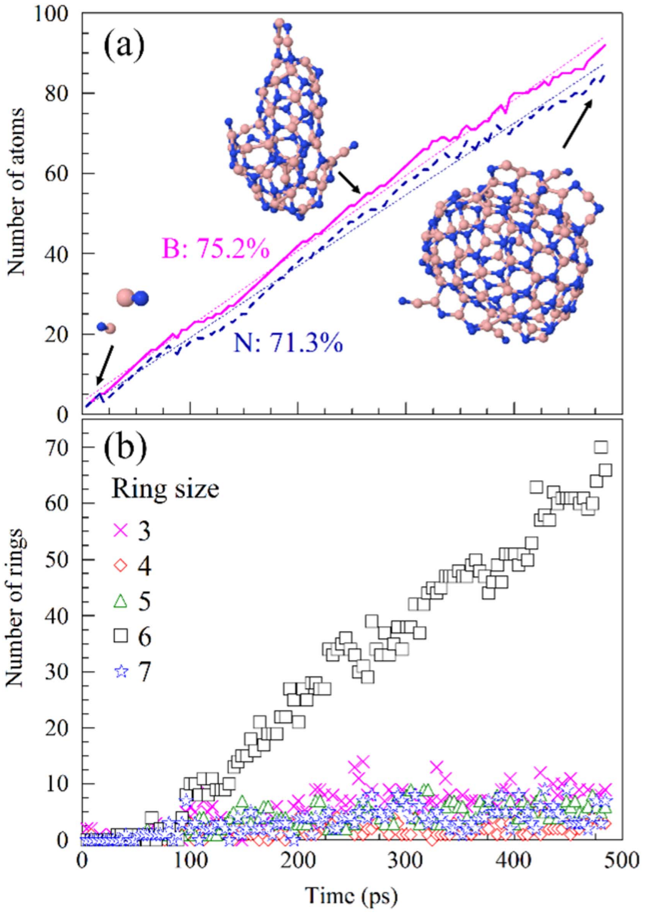

Figure 1. Formation of a BN nanocage by self-organization of BN diatomic molecules. Snapshots are taken at $t = 0$, $t = 264$ ps and $t = 480$ ps, respectively. The implantation rate is derived by linear regression. (a) Number of atoms and (b) number of rings are plotted as a function of time.

feedstock particles are emitted from random positions at a sphere of 3 nm radius surrounding the center of mass (CM) of the nanostructure-in-creation, by random initial angles and in the direction to the CM of structure.

3. Results and discussion

We present results for formation of a BN nanocage directly from BN diatomic atoms, formation of a nanoflake from an amorphous boron cluster bombarded by ammonium molecules (NH_3), and growth of a SWBNNT from a template bombarded by BN's, at high temperatures and concentrations, potentially available in the plasma volume of the electric arc at high pressure.

3.1. Nanocage formation

Figure 1 shows the formation of nanocage configuration. The logistics of the simulation is the following: (1) a single BN molecule is set in the center of a sphere of radius 3 nm. (2) Randomly from the surface of the sphere, BN are emitted toward the CM of the created structure, initially just BN molecule. Initial velocity of the CM of a BN 'projectile' is $\sqrt{3\,\mathrm{kT\,m^{-1}}}$, with $T = 2000$ K. (3) These emissions are repeated in intervals of 4 ps, with random angles of BN axis to the z-axis of the system. The whole system is kept at 2000 K by a Nose–Hoover thermostat. The sputtered particles in the process were removed from the system. The implantation of B and N is here undergoing together, shown in figure 1(a), although number of implanted N atoms is somewhat smaller than that of B because of occasional formation and ejection of N_2 molecules. The configuration at 264 ps seems to extend in one direction, indicating a possible BNNT growth, but with further feedstock of BN it rounds up to the nanocage. The formed polygons are dominated by hexagons already after 40 impacts of BN ($t = 160$ ps), shown by the black squares at figure 1(b), while other types of polygons (from triangles to heptagons) appear as 'noise'. The creation of the cage goes through a BN chain phase, followed by a flat flake phase, the 'tube' phase, and ends with a BN nanocage, as can be seen in the movie S1 of the online supplementary material. This case is very symptomatic for the process of BN-structures formation. To connect with the conditions in a volume of electric arc at $T = 2000$ K, we find that the simulation parameters above, lead to the concentration of BN of $\sim 1.6 \times 10^{18}\,\mathrm{cm}^{-3}$, i.e. to the partial BN pressure of $\sim$327 Torr.

3.2. Nanoflake formation

It is interesting to note that if we use NH_3 compounds in place of BN molecule as feedstock, with a small cluster of boron as target, a flat structure is formed via BN nanocage, as shown in figure 2 (see movie S2 of the online supplementary material). Since ammonia molecules are not stable at high temperatures, these molecules were created rovibrationally cold to retain their stability until hitting on the cluster surface, serving as feedstock of nitrogen and hydrogen. The implanted N atoms are consumed by B atoms in the cluster, forming a BN nanocage with H atoms chemisorbed on the surface. These H atoms destabilize the closed structure and lead to cage opening. Additional bombardment of NH_3 provide N feedstock for a perfect BN sheet of h-BNs with 1:1 ratio between B and N atoms, while H atoms only bond at the peripheries of the sheet. The implanted BN forms an open flat surface, which does not close since hydrogen atoms at the peripheries of the surface do not allow it. When this configuration is achieved, the implantation efficiency goes almost to zero, as shown in figure 2(a). Transitions of the system through different phases, including unstable closed-cage phase, are indicated in figure 2(b). The accumulation of H prevents the formation of a stable closed cage structure after 600 ps, similar as in the case of carbon nanostructure formation [28].

If a small boron cluster (six atoms) is 'fed' by HBNH, we also obtained a flake after about 1.2 ns, similar in appearance as in figure 2 with H atoms pointing outward. Even though there are feedstock of both B and N atoms that allow expansion of sheet infinitely, we did not observe a closure of sheet into cage or tube, since hydrogen atoms at the peripheries of the sheet do not allow it. Similar results have

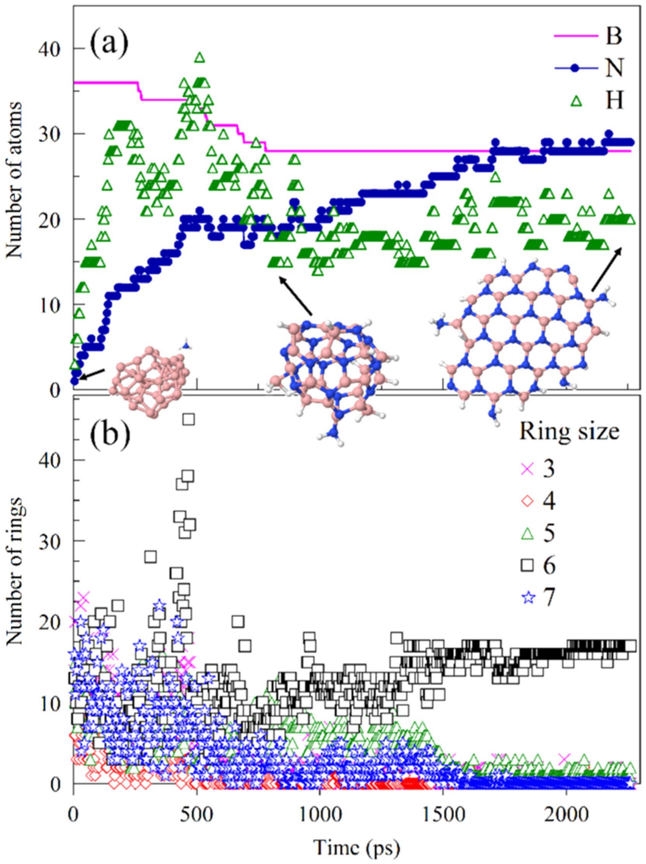

Figure 2. Evolution of B_{36} boron cluster irradiated by NH_3 molecules into the flat nanostructure. Three snapshots are taken at $t = 0$, $t = 800$ ps and $t = 2260$ ps, respectively. (a) Number of atoms and (b) number of rings are plotted as a function of time.

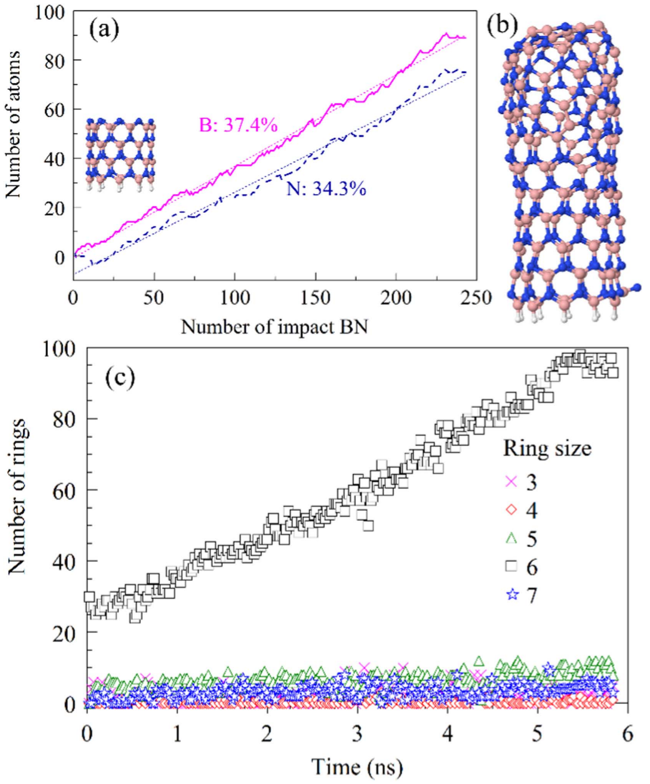

Figure 3. Growth of BNNT from a zig-zag template. (a) Increased number of atoms in BNNT as a function of impacted BN molecule number. The implantation rate is derived by linear regression. (b) Grown BNNT after 5.8 ns with 243 BN molecule feed. (c) Evolution of ring type during the growth.

followed when using BNH feedstock at 2000 K, i.e. a flat, flake like structure is formed like with HBNH feed. However, the same feed at 2500 K resulted into a cage structure, since a significantly smaller number of H atoms bonded than needed for pacifying the open, flat structure edges. We note that we could not get spontaneous self-organization into a nanostructure with H_2BNH_2, HBNH and NH_3 feedstocks like we were able with BN diatomic molecules. On the other hand, if a boron cluster is bombarded by H_2BNH_2 (suggested by Kim), the surface of cluster is quickly covered by H atoms, which greatly impede further implantation of feedstock molecules. Excess hydrogen atoms also prevent formation of BN hexagons. In such a case sp^3 configurations are mainly formed, rather than sp^2 that can evolve into a nanocage. The cage or fullerene structure is never formed.

3.3. BNNT growth

Most interestingly, we have succeeded to grow a BNNT from a short BNNT template, figure 3(a). (Online supplementary movie S3). Using a template (also called a seed) of a nanotube has been a common approach for the simulation of CNT growth [29, 30]. In our simulation, the BNNT template was created assuming ‘frozen’ hydrogen atoms at one of its ends, thus preventing rotation of the template and closing of the tube bottom upon BN impacts. The details of the simulation are the same as in obtaining nanocages in figure 1, with two significant differences: (1) the system is kept at elevated temperature of 2500 K, and (2) the BN feedstock was supplied every 24 ps, i.e. six times slower than in the case of the nanocage.

If any of these conditions was not fulfilled, the template upon BN supply is transformed slowly into the cage-like structure, with an open bottom. BN side chains are formed during the growth and they play important role. Growth of BNNT is completed by self-organization of BN side chains, which migrated and accumulated at the top end of the tube. If enough time is not provided for the migration of a chain to the top, the structure would grow to the side, where the chain would reorganize. Temperature and flux are two critical parameters for this process. The temperature of 2500 K is high enough to promote migration of the side chains, and also not too high to melt the structure. The lower flux of feedstock molecules guaranties enough time for migration of side chains to the top before new side chains can be created. With those two parameters optimized, the BNNT grows with few defects, as shown in figure 3(b), and as evidenced in figure 3(c) by the strongly dominating number of hexagon rings. These parameters correspond to the BN concentration of $\sim 2.4 \times 10^{17}\ \text{cm}^{-3}$, i.e. to the BN partial pressure of $\sim$62 Torr.

4. Conclusions

We note that, contrary to the widely accepted self-assembly mechanism, no boron nanoparticles are required in order to serve as nucleation point for BNNTs. In addition, our simulations question the widely held belief that the presence of atomic nitrogen is crucial to BNNS formation; rather, we find that the supply of feedstock containing already existing B–N bonds is important for the successful formation of BNNS structures with alternating B–N bonds. Although this is a result of our simulations, it might very well be that longer simulation time scales are required if individual B and N feedstocks are involved, which leads us to believe that feedstocks containing B–N bonds should be more efficient in the BNNS synthesis in general. Furthermore, we observe two similarities between SWBNNT formation and SWCNT simulations, as discussed for instance by Morokuma *et al* [31]. First, BN chain structures are the first to appear, and their subsequent branching and collapse form the basis of polygonal networks. Second, in agreement with SWCNT formation simulations, the feedstock supply times are crucial: the slower feedstock is added, the higher the chances for defect healing and the growth of ordered structures. We hope that our simulation efforts will serve as guidelines for the future highly efficient BNNS synthesis, based on the feedstock of BN molecules at appropriate density and temperature that would self-organize to the various BN nanostructures, dominantly of hexagons. Providing BN molecules in a gas phase, in the high-temperature and high-pressure plasma of an electric arc is an open challenge for the experimental plasma chemistry community.

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