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Boron-Based Nanostructures, Stability, Functionality and Synthetic Routes

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Abstract

Boron (B) is one of the most intriguing elements not only because of its position between metals and nonmetals in periodic table but also because of its ability to form an enormous number of allotropes. Apart from several bulk three-dimensional (3D) phases, boron can form 0D clusters, 1D nanotubes and nanowires, and 2D layers. In particular, boron sheets of monoatomic thickness have raised interest as a potential new 2D-material and as a (conceptual) precursor, for example, so-called α-sheets, from which other boron structures - fullerene cages and tubes - might be constructed. In fact, a number of planar B clusters up to tens of atoms, found in experiments, appear as seeds for extended sheets. In this project we developed theoretical methods to guide synthesis, have successfully identified the material substrates (Ag, Au, Cu) to producing the pure boron layers, and further even predicted what atomistic structures should be expected. These guidelines have successfully led to discoveries in several labs and now have grown into an active line of research worldwide.

Note: The initial project title "The Dawn of Boron Fullerenes—Key Issues of Stability and Synthetic Routes" has been changed during a renewal. We also note that earlier papers acknowledge the DOE Award ER46598, later changed numbering to DE-SC0001479.

Acknowledgement

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1 Introduction

Initial concept of B_{80} has motivated our interest and in fact fueled substantial research worldwide. It has exploded into hundreds of detailed studies of the family of large clusters, especially of hollow cages, their different isomers and chemically functionalized forms. Moreover, over the project years we could observe the “unfolding of the fullerene” in case of boron, akin to actual chronological developments in carbon research: first the Buckyball C_{60}, then carbon nanotubes, and then graphene. Similarly, boron hollow cages mapped onto planar geometries yield a variety of boron sheets, which promise their own important physical properties of electrical and thermal conductivity, polymorphism and glassy behaviors. While the theoretical studies progressed impressively fast, in experiments much fewer groups have attempted and yet less have succeeded in producing novel nanostructures. Boron chemistry is very different, in some respects more complex and its practicality is more challenging. Suffice it to mention that chemically uncombined boron is not found on Earth and pure forms are hard to produce industrially, or that precursors used to experiment with nanostructure synthesis are often toxic. Handling this in experimental lab, especially in academic setting, requires safety permits, certification etc. Our past and ongoing work resulted now, besides the research discoveries, in a capable facility for accelerated research of boron-based nanostructures. Our initially pure-boron research evolved while being influenced by concurrent broader developments in the research community. Within the emerging area of two-dimensional (2D) materials our project focus is on two important examples, representing in certain way two extreme cases: pure elemental B as most subtle and not synthesized (until 2015-2016), and *h*-BN—hexagonal boron nitride, a.k.a. “white graphene”—very stable compound, with the array of useful properties available for experiments. This compelled us to extend search to a *broad spectrum* of 2D boron-rich compounds whose synthesis can be rationalized, and properties explored in detail. We generalize our recently found approach, the first-principles computations of a layer-substrate system to offer a rational design of synthetic route for variety of 2D-compounds. Based on this approach we aimed to achieve, through theoretical modeling and experiments, both synthesis and property characterization of several boron-based nanostructures, primarily monolayers: pure B layers (including two-dimensional crystals of B_{12}) remain important lines of work; well-established stable *h*-BN; and novel layers of BC_3, BSi, B_2O_3, and B_xS_y composition. We mainly focused on 2D-materials, while also continued exploration of nanowires of pure B as well as coaxial B/BOx, already obtained in our labs, but calling for deeper characterization. Moreover, while pursuing our well planned quest, we will also kept an eye open for potential detection of the boron Buckyball hotly-debated isomers (now discovered in 2014), where serendipity remains a strong factor.

2 Theoretical studies of boron nanostructures

The 2D boron is shown to be polymorphic, with numerous local minima in a narrow energy interval above the ground line, in contrast to other 2D materials. Boron sheets are rich in multicenter bonding as a result of the electron deficiency of B atoms, making their structures fluxional, unlike for sp^2-bonded 2D materials. These features render the synthesis of 2D boron challenging.

Central line of our project effort was to perform theoretical studies (to parallele and eventually to guide experimental efforts) on the following aspects, reflected now in key publications: 2D boron polymorphism [1], as well as describe the proposed synthesis approach [2] and further explore the role of selected feasible metal substrates [3].

2.1 Polymorphism of two-dimensional boron [1]

The structural stability and diversity of elemental boron layers are evaluated by treating them as pseudoalloy $B_{1-x}[]_x$, where [] is a vacancy in the close-packed triangular boron lattice. This approach allowed for an elegant use of the cluster expansion method in combination with first-principles density-functional theory (DFT) calculations, leading to a thorough exploration of the configurational space, as presented in Fig. 1(a). A finite range of compositions *x* is found where the ground-state energy is essentially independent of *x*, uncovering a variety of stable B-layer phases (all metallic), some of which are shown in Fig. 1(b), and suggesting polymorphism, in stark contrast to graphene or hexagonal boron nitride, or any other 2D material.

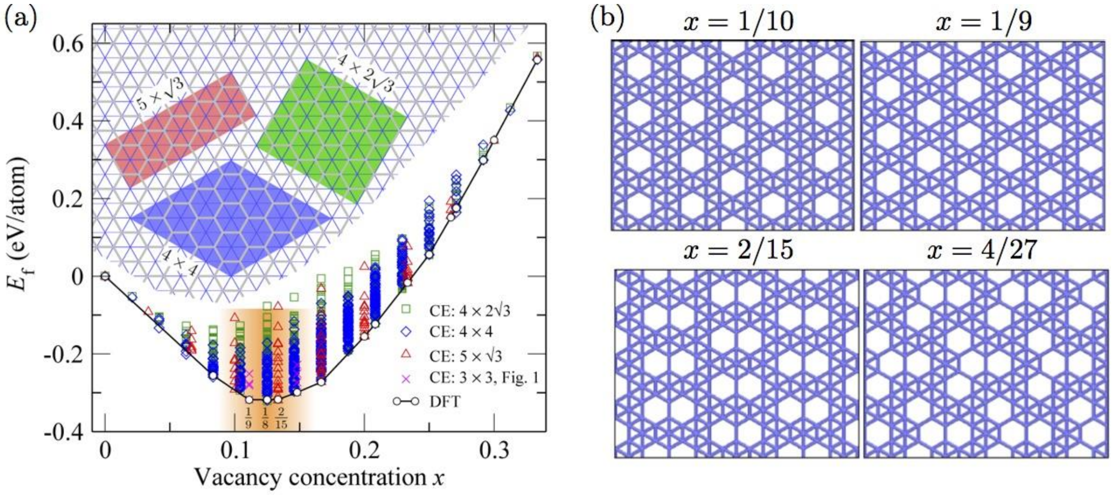

Figure 1: (a) Formation energies E_f of all ≃2100 symmetry-inequivalent structures calculated from cluster expansion method fits to ≃130 configurations calculated with DFT for the three supercells in the inset. (b) Some of the most stable B layers in the range of $x \simeq 0.1$–0.15.

2.2 Probing the synthesis of two-dimensional boron by first-principles computations [2]

Finding that all boron sheets-polymorphs are higher in energy than its 3D-crystal form posed a challenge to theory, to assess any possibility of creating such metastable 2D crystals. Generally, the synthesis of novel two-dimensional materials has attracted considerable interest because of their various unique properties. While the production of 2D boron (^{2D}B) sheets remained a challenge, it was important to theoretically investigate the possible fabrication methods. Threfore, at that stage of th eproject, we explored the formation of B sheets on metal (Cu, Ag, Au) and metal boride (MgB_2, TiB_2) substrates using first-principles calculations. Our results suggest that B sheets can be grown on the

Ag(111) or Au(111) surfaces by deposition. B atoms decomposed from a precursor, and driven by the gradient of the chemical potential, will assemble into 2D clusters and further grow into a larger sheet, while formation of three-dimensional boron (^{3D}B) structures could be impeded owing to a high nucleation barrier. In addition, saturation of a boron-terminated MgB_2 surface in a boron-rich environment can also lead to the formation of B sheets. These sheets are weakly bound to the substrates, suggesting a feasible post-synthetic separation into the free-standing forms. Our work proposed feasible approaches to synthesize ^{2D}B, presented in Fig. 2, and could possibly pave the way towards its application in nanoelectronics. In fact, 2 years later these recommendations of using Ag(111) has been followed in discovery-experiments, in Argonne Lab – Northwestern U collaboration, and independently in the Institute Academy of CAS, Beijing.

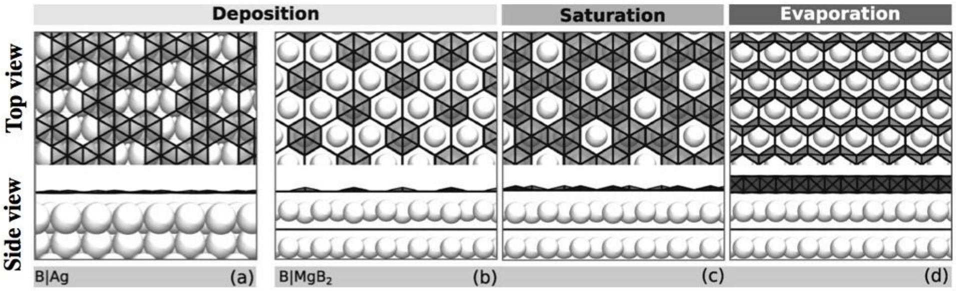

Figure 2: Atomic structure of B sheets, representing different synthetic methods: deposition on metals (a) and metal-terminated surface of borides (b), saturation of B-terminated surface of borides (c), and evaporation of borides (d). Ag and MgB_2 are shown as representatives for metals and metal borides, respectively.

2.3 Two-dimensional B-monolayers mediated by metal substrates [3]

Two-dimensional materials, such as graphene and boron nitride, have specific lattice structures independent of external conditions. In contrast, the structure of 2D boron sensitively depends on metal substrate, and so it was important to determine what mus be expected in potential deposition-snthesis (cannot be derived from earlier screening on vacuum!) Using the cluster expansion method and a newly developed surface structure-search method, both based on first-principles calculation, we performed this extensive computational investigation. The ground-state structure of 2D B on Ag or Cu obtained with a newly developed surface reconstruction prediction method based on particle swarm optimization is shown in Fig. 3(a,b). The preferred 2D B on weaker interacting Au is slighly nonplanar with some buckling and numerous polymorphs as in vacuum, whereas on more reactive Ag, Cu, and Ni, the polymorphic energy degeneracy is lifted and a particular planar structure is found to be most stable. We also show that a layer composed of icosahedral B_{12} is unfavorable on Cu and Ni but unexpectedly becomes a possible minimum on Au and Ag, as demonstrated in Fig. 3(c). The substrate-dependent 2D boron choices originate from a competition between the strain energy of buckling and chemical energy of electronic hybridization between boron and metal. Again, this predicted structure of Fig. 3a is now observed experimentally, although general determination of the lattices remains a subject of ngoing research inseveral labs.

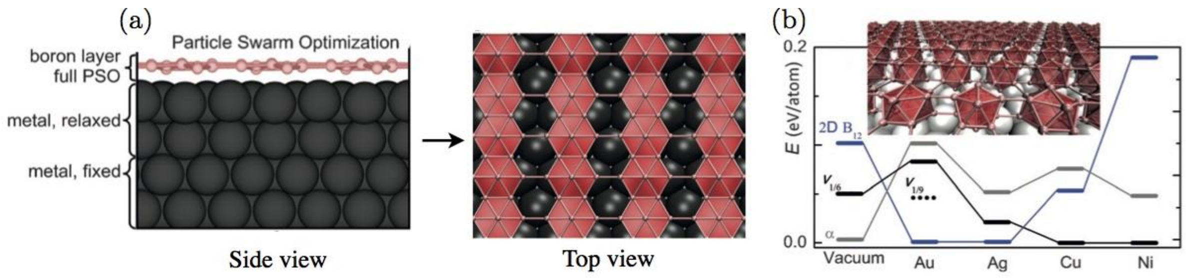

Figure 3: (a) The predicted ground-state structures of 2D B on Ag or Cu obtained using the slab model with particle swarm optimization method. (b) Energy order of the α-sheet, $v_{1/6}$-sheet, and the B_{12} layer in vacuum and on metals. Inset: the atomic configuration of the B_{12} layer on Ag.

3 Experimental study of boron nanostructures

These experimental efforts, early in he project, have been valuable by demonstrating great challenge of growing B nanostructres by CVD, in both choice of (often toxic) precursors and also choice of substrates and conditions. Boron, carbon's neighbor on the periodic table, has one of the most complex and rich chemical behaviors among all the elements due to its electron deficient nature. Similar to carbon, boron is capable of forming stable covalently-bonded molecular networks and its crystal forms, including amorphous boron, are distinct from any other element because boron clusters are the fundamental building blocks. The pure boron nanostructures have attracted considerable attention because of their potential applications in nano-electronics, and sensor devices. Earlier, syntheses of boron nanotubes have been reported (Yale University) but their structures have not been confirmed to be what theoretical models predicted. Synthesis of boron fullerenes and 2D layers still remained a challenge in laboratories (now B40 being produced in 2014, Brown University), though recently various approaches have led to the synthesis of many boron nanostructures such as nanoparticles, nanowires, nanoribbons, and nanocones. Our early work on the synthesis of boron layers proved indeed to be challenging, with CVD methods never yieldind desirable crystal lattice. Instead, we succeeded to produce amorphous boron nanowires using a simple thermal vapor phase mass transfer method [4].

3.1 Synthesis and photocurrent of amorphous boron nanowires [4]

Although theoretically feasible, synthesis of boron nanostructures is challenging due to the highly reactive nature, high melting and boiling points of boron. We have developed a thermal vapor transfer approach to synthesizing amorphous boron nanowire using a solid boron source, see Fig. 4. The amorphous nature and chemical composition of boron nanowires were characterized by high resolution transmission electron microscopy, selected area electron diffraction, and electron energy loss spectroscopy. Optical properties and photoconduction of boron nanowires have not yet been reported. In our investigation, the amorphous boron nanowire showed much better optical and electrical properties than previously reported photo-response of crystalline boron nanobelts. When excited by a blue LED, the photo/dark current ratio (I/I_0) is 1.5 and time constants in the order of tens of seconds. I/I_0 is 1.17 using a green light.

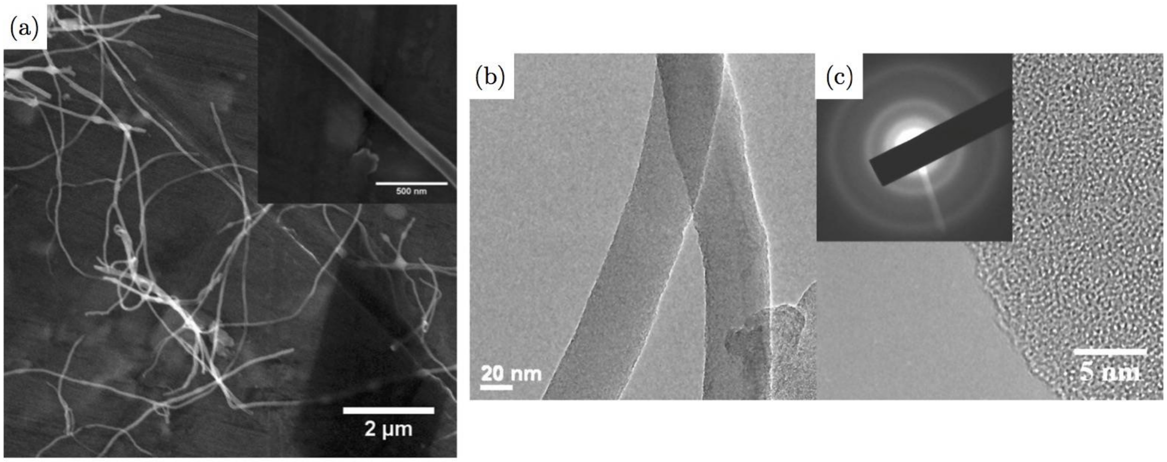

Figure 4: (a) Scanning electron microscopy (SEM) micrograph of boron nanowires deposited on Si wafer substrate after sonication. Inset shows the detail of a single boron nanowire. (b) Transmission electron microscopy (TEM) micrograph of boron nanowires. The diameter is about 40 nm. (c) Typical high-resolution TEM (HRTEM) micrograph of boron nanowires. No crystalline fringes can be identified at atomic scale.

4 Studies of h-BN, and other emergent nanostructures

Boron nitride (BN) is a wide band gap III-V compound with remarkable physical properties and chemical stability. Hexagonal BN (h-BN) is comprised of alternating boron and nitrogen atoms in a honeycomb arrangement, consisting of sp^2-bonded two-dimensional layers. Within each layer of h-BN, boron and nitrogen atoms are bound by strong covalent bonds, whereas the layers are held together by weak van der Waals forces, as in graphite. Therefore, h-BN films could be peeled off from bulk BN crystal by micromechanical cleavage and used as a dielectric layer. Few-layer h-BN has also been made by ultrasonication and high-energy electron beam irradiation of BN particles. The chemical decomposition reactions of various precursors have been used to demonstrate the growth of single layer BN domains over small areas. However, methods for preparing good quality h-BN layers over large areas would bring new opportunities to exploit its properties and potential applications, especially as interesting two-dimensional dielectric material in graphene-based electronics.

We investigated numerous aspects of BN nanostructures theoretically by performing computations [6-11], as well as experimentally [5, 12-16]. Besides, we also studied several important yet secondary to this project materials, as the tasks emerged with our progress in main directions. Not discussed here in detail are studies of magnesium boride nanotubes [17], hydrogen-storage in sorption materials [18], 2D transition metal dichalcogenide binary alloys [19], feasibility of lithium storage on graphene [20] at the level of computations, as well as performed numerous experiments on graphene films [21-23] and carbon nanotube films [24]. Here we report in somedetails only a fraction of our experimental [5] and theoretical [6, 7] studies on BN nanostructures, as closest to pure B composition, and of their own recognized importance.

4.1 Large scale growth and characterization of atomic h-BN Layers [5]

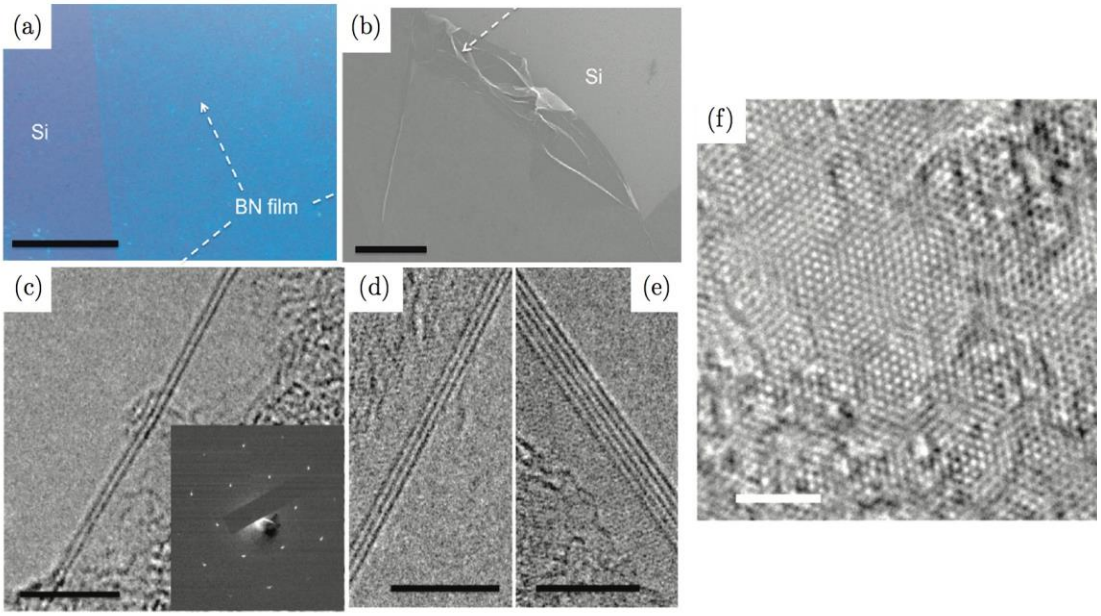

Figure 5: Topography of ultrathin hexagonal BN films: (a) photograph of a large h-BN film on a silicon substrate, where scale bar is 1 cm; (b) SEM image shows a h-BN film (scale bar 10 μm). Microstructure of atomic layers hexagonal BN: (c) HRTEM images of the film edges indicate that the h-BN are two atomic layers thick. Some of as-grown films are three to five layers (d, e), where the scale bar is 5 nm. The insert of (c) shows the hexagonal structure of h-BN film. (f) A typical atomic image of a h-BN films, where the scale bars is 2 nm.

Hexagonal boron nitride, a layered material similar to graphite, is a promising dielectric. Monolayer h-BN, so-called "white graphene", has been isolated from bulk BN and could be useful as a complementary two-dimensional dielectric substrate for graphene electronics. In this effort, which has become a seminal paper (now >1,000 citations and growing), we report the large area synthesis of h-BN films consisting of two to five atomic layers, using chemical vapor deposition. These atomic films show a large optical energy band gap of 5.5 eV and are highly transparent over a broad wavelength range. The mechanical properties of the h-BN films, measured by nanoindentation, show 2D elastic modulus in the range of 200–500 N/m, which is corroborated by corresponding theoretical calculations.

4.2 h-BN with “colorful” edges: The energies and morphology [6]

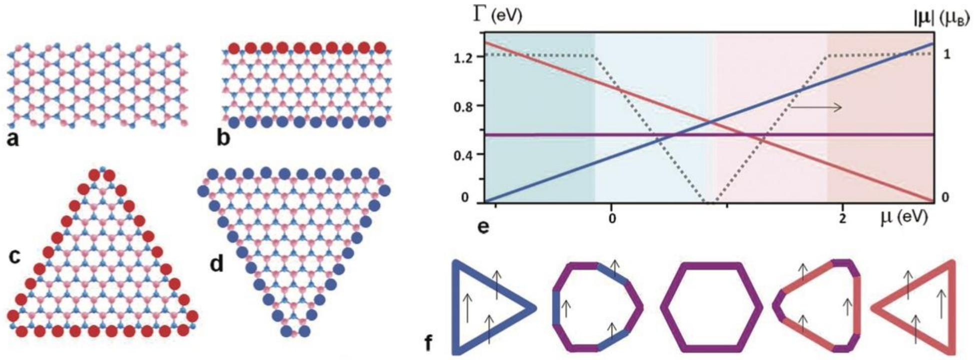

Figure 6: Relaxed geometries of selected BN structures with boron atoms red and nitrogen blue: (a) an armchair ribbon, note the edge N-atoms buckle out; (b) zigzag ribbon, highlighted B and N at the opposite edges; (c) B-rich triangle and (d) N-rich triangle. (e) The energies for the boron-rich zigzag (ZB/C, red), armchair (A/C, purple) and nitrogen-rich zigzag (ZN/C, blue) interfaces with graphene (C), as a function of chemical potential μ of B. Dotted line shows the magnetism, per unit of perimeter, in Bohr magnetons μB, as it changes along with the equilibrium shape of graphene inclusions shown in (f), here thin arrows length is proportional to the magnitude of magnetism.

Interfaces play a key role in low dimensional materials like graphene or its boron nitrogen analog, white graphene. The edge energy of h-BN has not been determined as its lower symmetry makes it difficult to separate the opposite B-rich and N-rich zigzag sides. We reported unambiguous energy values for arbitrary edges of BN, including the dependence on the elemental chemical potentials of B and N species, as shown in Fig. 6. A useful manifestation of the additional Gibbs degree of freedom in the binary system, this dependence offers a way to control the morphology of pure BN or its carbon inclusions and to engineer their electronic and magnetic properties.

4.3 Growth mechanism and morphology of hexagonal boron nitride [7]

h-BN sheet is a structural analogue of graphene, interestingly boron-rich, yet its growth mechanism has been rarely studied, as complicated by its binary composition. In this project task, we revealed an atomistic growth mechanism for the h-BN islands by combining crystal growth theory with comprehensive first-principles calculations. The island shapes preferred by edge equilibrium are found to be inconsistent with experimental facts, which is in contrast to previous common views. Then the growth kinetics was explored by analyzing the diffusion and docking of boron and nitrogen atoms at the edges in a step-by-step manner of the nanoreactor approach, see Fig. 7. The determined sequence of atom-by-atom accretion reveals a strong kinetic anisotropy of growth. Depending on the chemical potential of constituent elements, it yields the h-BN shapes as equilateral triangles or hexagons, explaining a number of experimental observations and opening a way for the synthesis of quality h-BN with controlled morphology. The richer growth kinetics of h-BN compared to graphene is further extendable to other binary two-dimensional materials, notably metal dichalcogenides.

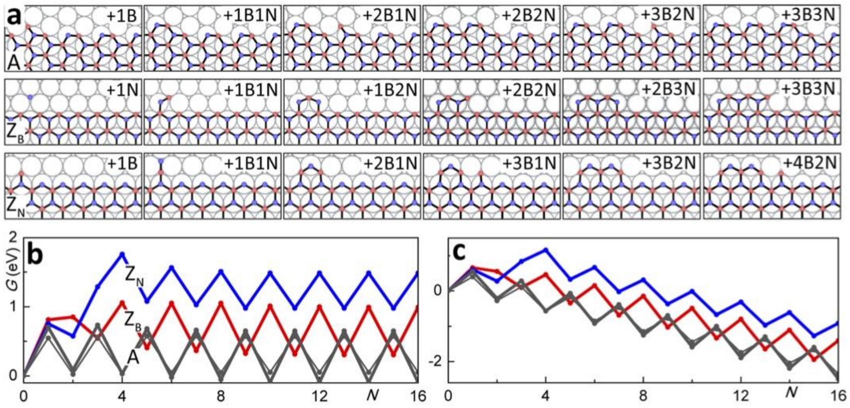

Figure 7: Kinetic models of h-BN growth on Ni. (a) Optimal atomic configurations during the docking of B and N monomers to the armchair (A, top), B-terminated zigzag (ZB, middle), and N-terminated zigzag (ZN, bottom) edges at chemical potential for B of μ_B = -0.5 eV. (b,c) Corresponding free energy evolution at $\Delta\mu_{BN}$ = 0.01 (b) and 0.3 eV (c).

5 Conclusions

This project has demonstrated the importance of theory guidance to the experimental quest for novel materials in general. Pure boron nanostructures provided an excellent learning example of that. Indeed, in the course of this project we have seen evolution from early predictions of boron fullerenes towards rich study of their structures, and eventual experimental detection of B-cage cluster (in another laboratory). In even stronger line of our work, the possibility and variability of 2D-boron was predicted, the specific substrates being recommended, and the structure of the sheet predicted through extensive computational search. This eventually has culminated in experimental synthesis in the independent labs internationally. Current main challenges are in separation of 2D-boron from metallic substrates, for any deeper physical characterization or borophene utility. Alternatively, it remains compelling to find possibility of synthesis on non-metallic substrates and with chemical vapor deposition process.

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