

Electronic supplementary information for  
**Hydrogen-assisted Growth of Single Crystalline Borophene Investigated by  
First-principles Calculations**

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**FIG. S6:** Binding energy of atomic H on high symmetric adsorption sites on B<sub>44</sub>/Ag.

**FIG. S7:** Local projected charge density and density of states analysis.

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## I: Calculation details.

A Ag(111)  $4\sqrt{3} \times 8$  supercell including five atomic layers was used to simulate the Ag substrate with a vacuum layer of more than 15 Å in the z-direction to ensure the decoupling between the neighboring images. An energy cutoff of 400 eV and  $3 \times 3 \times 1$  Monkhorst Pack k-point mesh were adopted for the calculations. During the optimization processes, the bottom two layers of Ag atoms were fixed to their bulk positions, and the top three layers were fully relaxed until the residual forces on each atom are smaller than 0.02 eV/Å. The van der Waals (vdW) correction was confirmed to possess negligible effect on the experimental results of both the bulk lattice constants and adsorption sites and diffusion barrier of the B atoms on Ag(111). Thus, vdW correction is no longer considered in the following simulations. The Bader charge analysis is adopted to analyze the charge transfer. To investigate the kinetic processes, the climbing image nudged elastic band (CI-NEB) [1, 2] method was used to identify the transition states and minimum energy paths (MEPs).

## II: The preferred adsorption of a B monomer on the Ag(111) substrate.

Four high-symmetry surface sites (*top*, *fcc* hollow (*fcc*), *hcp* hollow (*hcp*), and *bridge*) and one subsurface octahedral (*oct*) site are considered as the initial adsorption positions of the B monomer, following with extensive optimizations. As shown in FIG. 1(a) of the manuscript, it is found that, energetically, the B monomer prefers the subsurface *oct* site, which is 0.782 eV lower than that on the meta stable surface *fcc* site. Note that, the B monomer cannot be stably adsorbed on the *hcp* site, from where it will be readily relaxed to the subsurface *oct* site right below the *fcc* site, upon overcoming a negligible activation energy barrier ( $E_{\text{bar}}$ ).

**FIG. S1:**

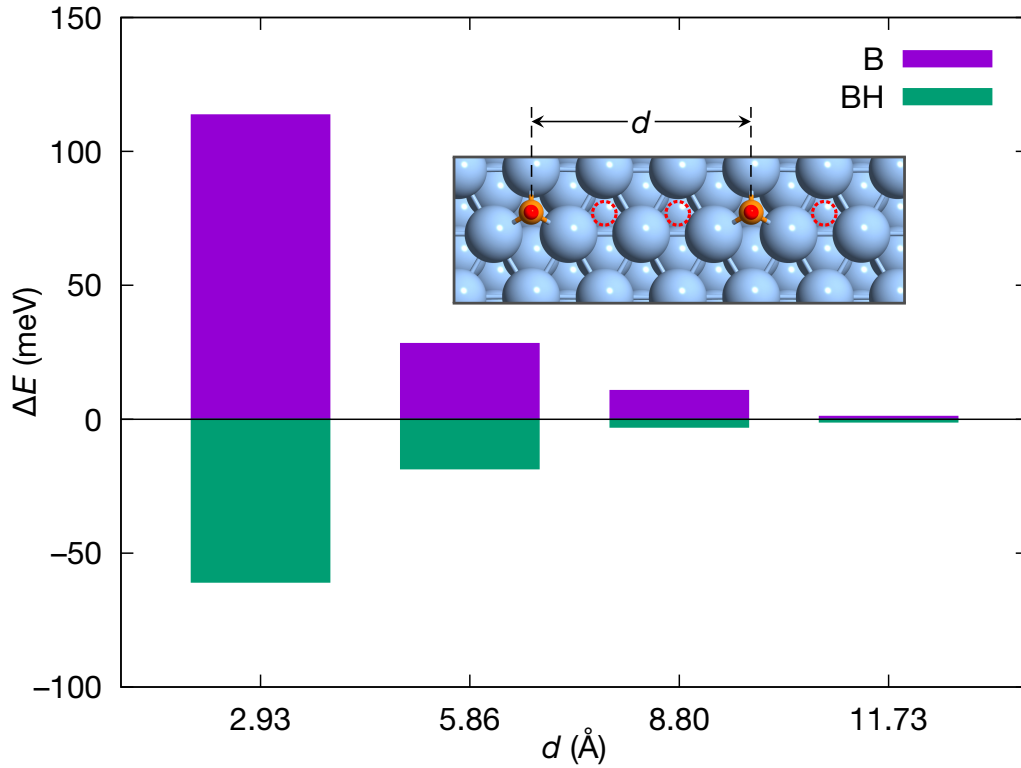


FIG. S1. Relative energies of the two B (BH) atoms (molecules) in two subsurface *oct* sites (on surface *fcc* sites) as a function of B-B distance.

From FIG. S1, one can see that, the larger the B-B distance of the two B atoms in the subsurface *oct* sites (denoted as the dotted cycles) of the Ag(111) substrate is, the lower the total energy of the  $B_2/Ag(111)$  complex is, indicating the repulsive pairwise interaction feature of the two B atoms on the Ag(111) surface, which prevents the B atoms from nucleation. However, for the two BH molecules on the surface *fcc* sites, the larger the B-B distance is, the higher the total energy of the  $(BH)_2/Ag(111)$  complex becomes, indicating the attractive pairwise interaction feature of the two BH molecules, which facilitate the B atoms nucleation.

FIG. S2:

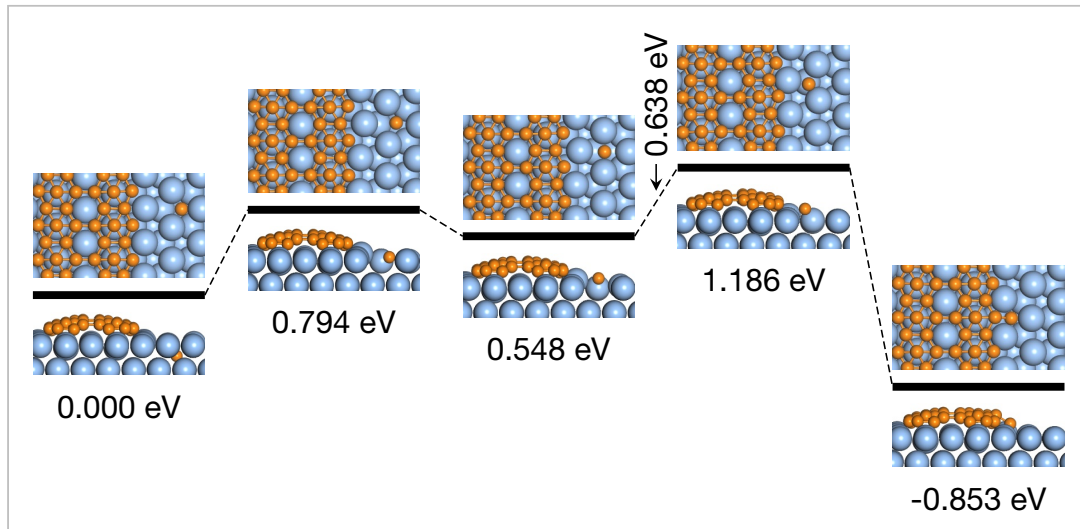


FIG. S2. Minimum energy pathway for a B atom attaching to the borophene nanoribbon from the subsurface *oct* site.

From FIG. S2, one can see that in the process of one B atom attaching to the borophene nanosheet from the subsurface *oct* site, the B atom first overcomes an  $E_{\text{bar}}$  of 0.794 eV to diffuse from the *oct* site to vicinity of the surface *fcc* site; then the surface B atom continue to overcome an  $E_{\text{bar}}$  of 0.638 eV to attach on the edge of the borophene growth.

**FIG. S3:**

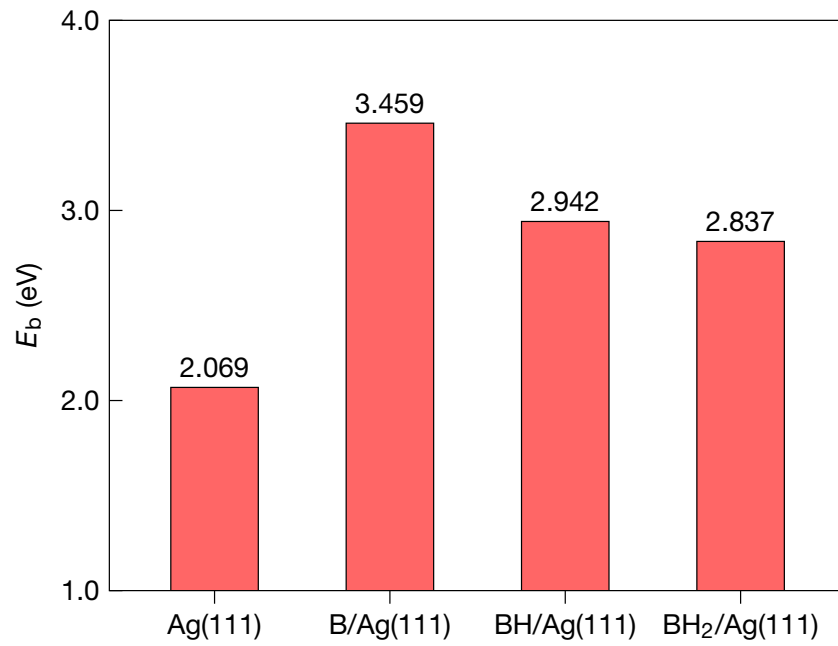


FIG. S3. Binding energy ( $E_b$ ) of atomic H on Ag(111), B/Ag(111), BH/Ag(111), and BH<sub>2</sub>/Ag(111) substrates.

In FIG. S3,  $E_b$  was defined as  $E_b = -(E_{\text{tot}} - E_{\text{sub}} - E_{\text{H}})$ , where  $E_{\text{tot}}$ ,  $E_{\text{sub}}$ , and  $E_{\text{H}}$  are the total energies of the H/substrate complex, substrate, and the atomic H, respectively. Except for in the case of Ag(111), the H atoms are adsorbed on the B reactive sites.

FIG. S4:

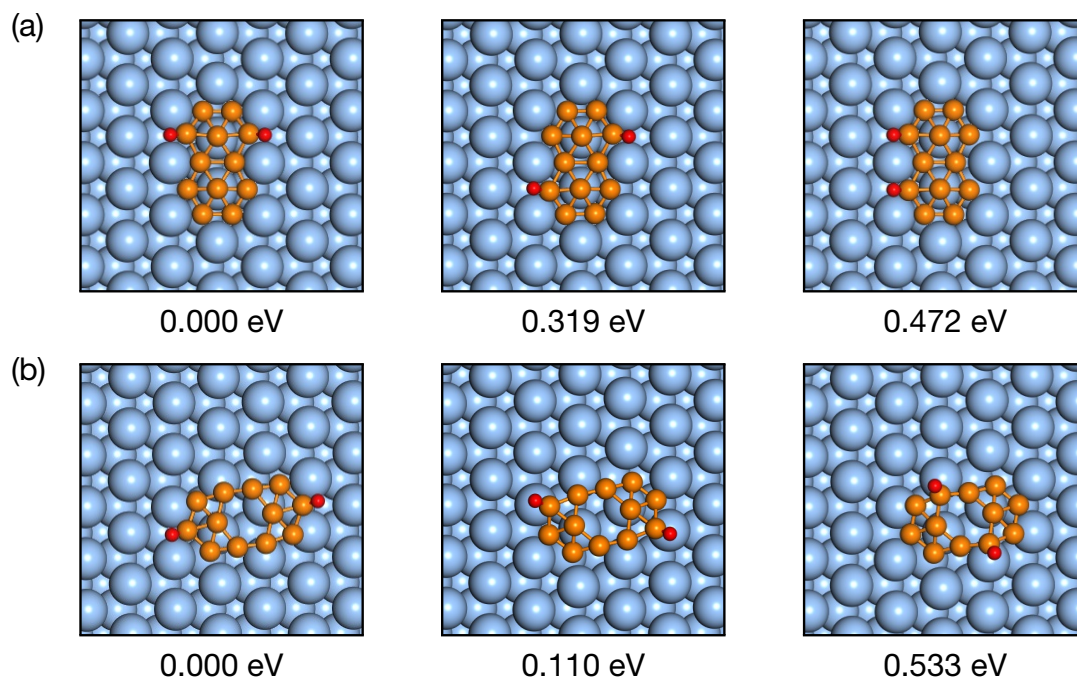


FIG. S4. Relative energies of the representative low-lying isomers of  $B_{12}H_2$  species. (a)  $\beta_{12}$ . (b)  $\chi_3$ .

Here, we performed extensive structure searching to identify the most stable configurations of the  $\beta_{12}$ - $B_{12}H_2$  and  $\chi_{12}$ - $B_{12}H_2$  structure on Ag(111) substrate, with the relative energies of the representative low-lying isomers presented in FIG. S4.

FIG. S5:

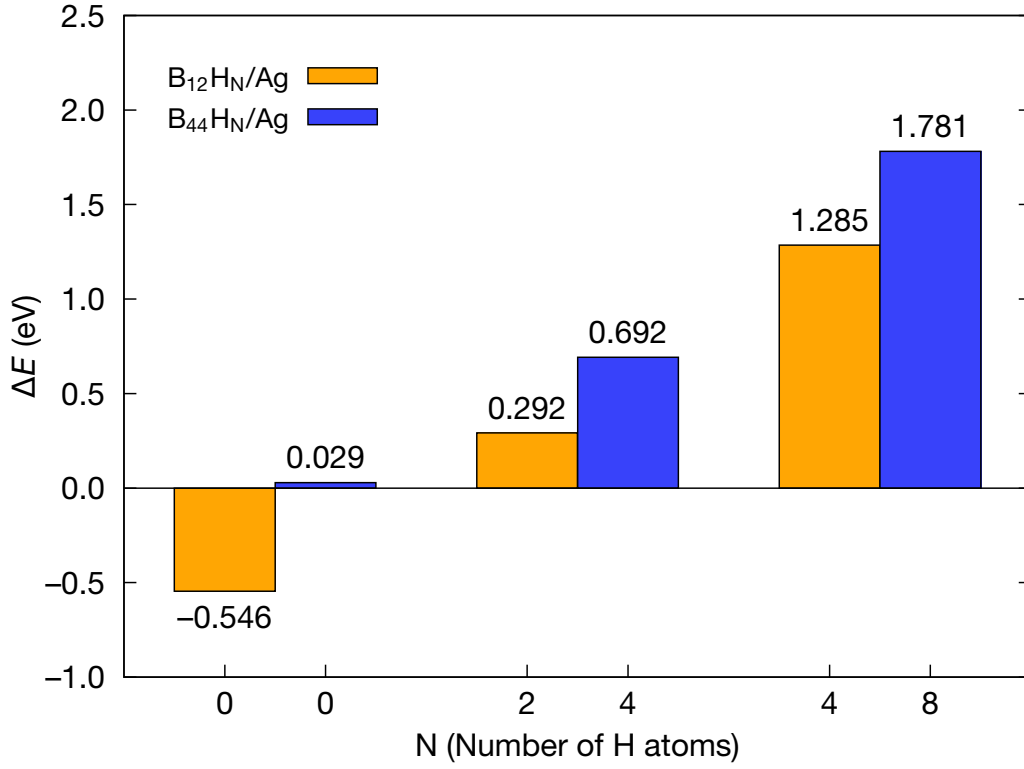


FIG. S5. Relative energies of the  $B_M H_N / \text{Ag}(111)$  ( $M = 12, N = 0, 2, 4$ ;  $M = 44, N = 0, 4, 8$ ) complexes between  $\beta_{12}$  and  $\chi_3$  phases, i.e.,  $\Delta E = E(\chi_3) - E(\beta_{12})$ .

From FIG. S5, one can see that relative stability of the two stable borophene phases can be effectively lift via controlling the content of hydrogen.

FIG. S6:

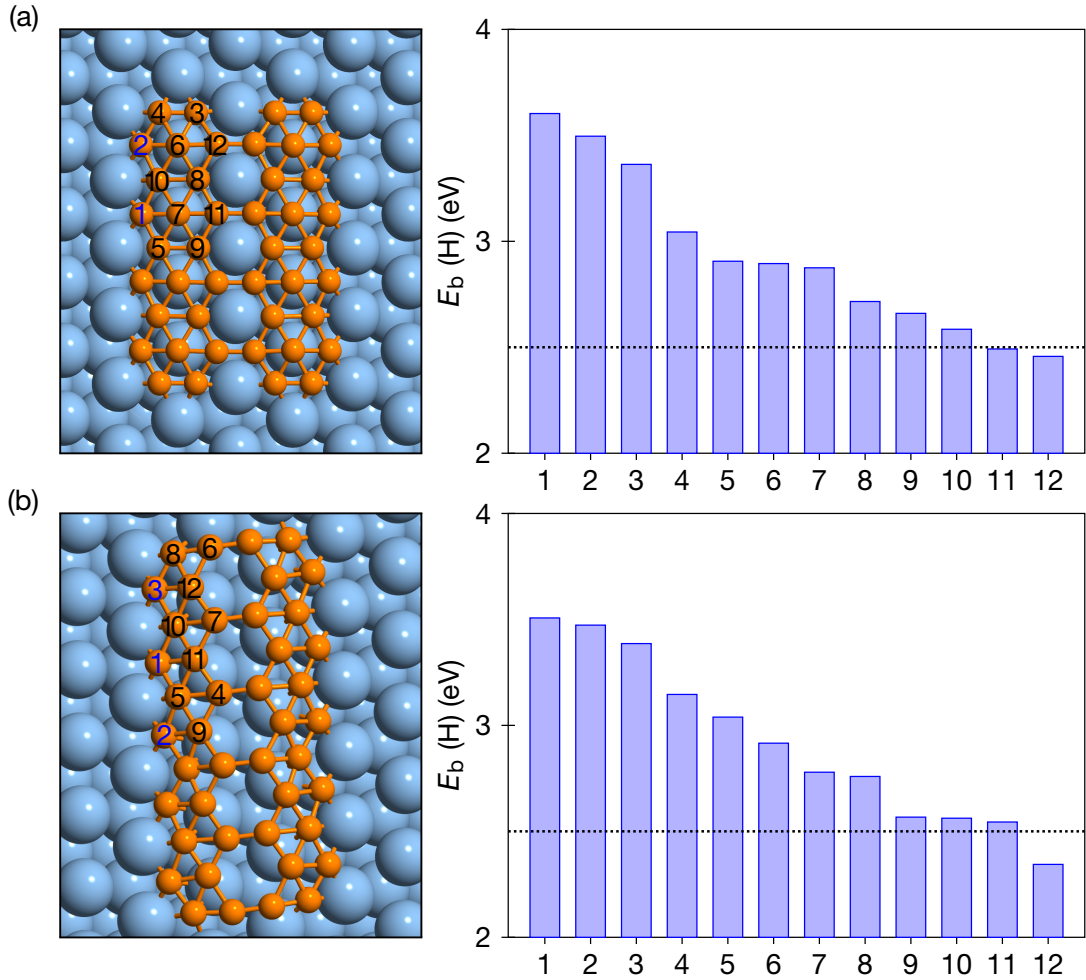


FIG. S6. Binding energy of atomic H on high symmetric adsorption sites on  $\beta_{12}$  (a) and  $\chi_3$  (b) phases of  $B_{44}/Ag$ . The dashed line represents the calculated  $E_b$  of H atoms on the top site of borophane [3], wherein the hydrogen can be reversibly adsorbed and desorbed.

In FIG. S6, we present all the possible adsorption sites and its corresponding binding energies of the H atoms in consideration of the symmetry. Here, we numbered the adsorption sites, with the sequence of number 1 as the one with the largest  $E_b$ , and so on. One can see that, overall, the edge B atoms possess the largest  $E_b$  for H adsorption, and the central surface B atoms possess relatively low  $E_b$ , demonstrating that the H atoms will preferentially saturate the edge sites.



FIG. S7:

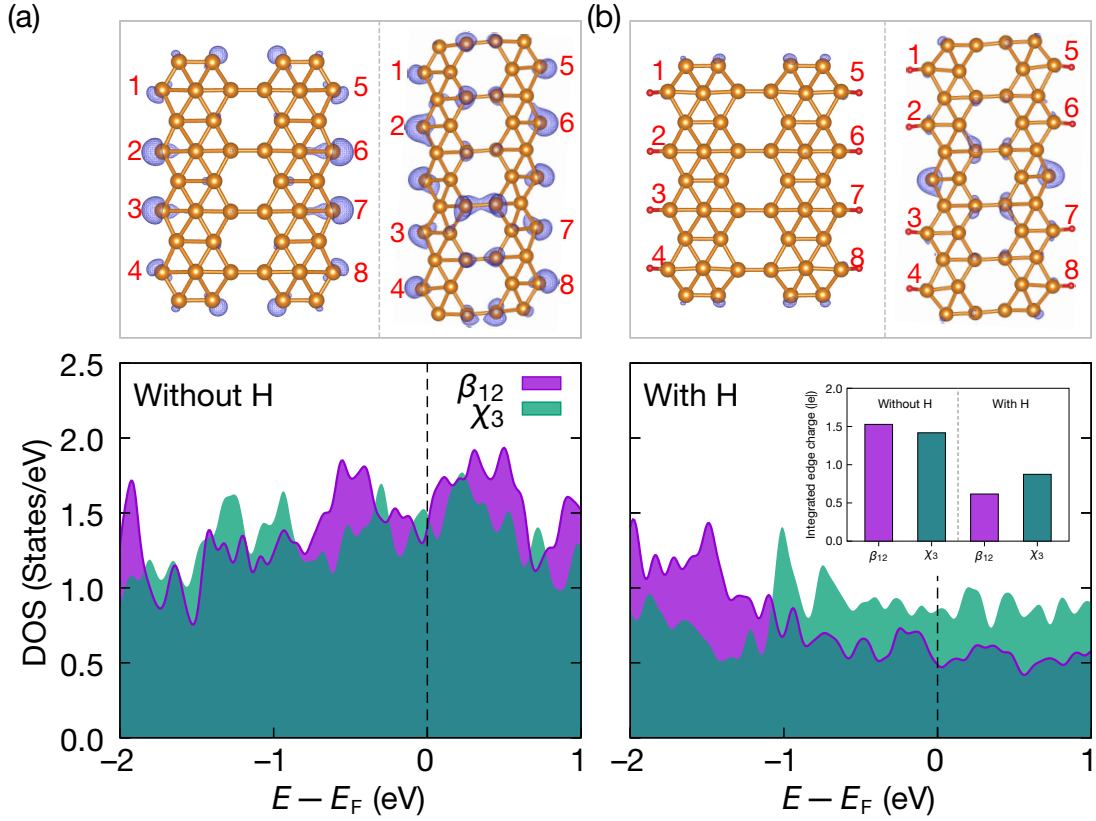


FIG. S7. Local projected charge density (top panels) and density of states (DOS) (bottom panels) analysis. (a) B<sub>44</sub>, (b) B<sub>44</sub>H<sub>8</sub>.

In FIG. S7, we present Local projected charge density (top panels) and density of states (DOS) (bottom panels) analysis. (a) B<sub>44</sub>, (b) B<sub>44</sub>H<sub>8</sub>. For the charge density, the energy range is selected from -0.5 to 0.0 eV (Fermi level), with an isosurface of 0.005 e/Å<sup>3</sup>; The DOS are projected on the four representative numbered edge atoms. The integrated edge charges in the selected energy range are comparatively shown in the inserted figure.

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- [1] G. Henkelman and H. Jónsson, Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points, *J. Chem. Phys.* **113**, 9978 (2000).
- [2] G. Henkelman, B. P. Uberuaga, and H. Jónsson, A climbing image nudged elastic band method for finding saddle points and minimum energy paths, *J. Chem. Phys.* **113**, 9901 (2000).
- [3] Q. Li, C. Kolluru Venkata Surya, S. Rahn Matthew, E. Schwenker, S. Li, G. Hennig Richard, P. Darancet, K. Y. Chan Maria, and C. Hersam Mark, Synthesis of borophane polymorphs through hydrogenation of borophene, *Science* **371**, 1143 (2021).