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Article

First-Principles Study on the Oxidation of Supported β_{12} -Borophene

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ABSTRACT: The oxidation stability of borophene is deemed as a prerequisite for its broad applications; however, there is a contradiction from experiments as to whether boron atoms in borophenes are active or inert to oxidation. Our detailed density functional theory calculations performed herein indicate that O₂ molecules tend to be chemisorbed on supported β_{12} -borophene easily and dissociate into separated atoms by overcoming very low barriers, and spin triplet-to-singlet conversion is not important in the chemisorption process. It is found that O₂ molecules prefer to be adsorbed on two hexacoordinated boron atoms and then dissociate and diffuse along filled-hexagon ribbons. A comparison between our calculated core-level binding energies and the experimental X-ray photoelectron spectroscopy, in combination



with detailed kinetic analyses, indicates that boron atoms in supported borophenes are active rather than inert to oxidation. This conclusion is further supported by a novel B_5O_4 sheet model calculation. The results on the oxidation stability and mechanism suggest the protection of borophenes from oxygen is therefore essential for their broad applications.

INTRODUCTION

Boron has drawn considerable attention in the past few years due to not only its rich chemical diversity but also its similarity to carbon. The promising properties of graphene¹⁻³ stimulate great interests in other two-dimensional (2D) materials, such as BN monolayer,⁴ silicon monolayer,⁵ and boron monolayer^{6,7} (termed borophene⁸). Because of multicenter bonding, a lot of freestanding borophene allotropes with competitive cohesive energy were proposed.^{9,10} Borophenes were finally synthesized on Ag(111) substrate for the first time^{11,12} recently, and subsequently, other borophene allotropes (e.g., honeycomb borophene) on silver and other substrates^{13,14} were successfully realized. Since the successful synthesis of borophenes, the exploration on its potential applications seems to be of great demand. Theoretical studies suggested that borophenes were promising electrode materials for Li-ion and Na-ion batteries, which had the highest capacity among all the 2D materials discovered to date.¹⁵ In addition, it was revealed that borophenes showed remarkable mechanical characteristics, such as very high flexibility, ideal strength, and a negative Possion's ratio.^{16–18} Isolated nickel atoms supported on β_{12} borophene were predicted to be single-atom bifunctional catalyst for overall water splitting.¹⁹

As the prerequisites for the broad applications of borophenes, besides exfoliation,²⁰ oxidation stability is of critical importance as well. Feng et al. claimed that the borophenes were oxidized from their edges, and the boron atoms inside the islands were quite inert to oxidation; the ratio of oxidized to unoxidized boron atoms is small (about 0.23) even with long exposure to

air.¹² However, such a ratio close to one-quarter seems hard to be achieved if only the edge atoms are oxidized. Furthermore, Mannix et al. reported that bare borophenes were partially oxidized within several hours in ambient conditions, and the borophenes would be oxidized in several weeks even with the protection of an amorphous silicon/silicon oxide capping layer.¹¹ It was also reported that boron films with thicknesses of \leq 45 nm exhibit pronounced degradation upon air exposure,²¹ which indicated noticeable chemical activity of borophenes to oxidation given the quantum size effect and large electronegativity difference between oxygen and boron (i.e., 1.4).

It was reported that the electronic and optical properties of triangular borophene (i.e., δ_6) could be tuned by adsorbing oxygen atoms.^{22,23} Guo et al. investigated the oxidation of freestanding δ_6 -borophene and claimed that the oxidation of the borophene strongly depended on the spin triplet-to-singlet conversion.²⁴ Another group drew a similar conclusion for freestanding δ_6 -borophene, but the spin triplet-to-singlet conversion was not observed upon the presence of an Ag(111) substrate;²⁵ however, how the triplet O₂ molecule converted to the singlet state when getting close to the substrate maintained unclear. Another study investigated the oxidation of

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supported χ_3 -borophene, but the study neglected the spin triplet-to-singlet conversion,²⁶ while the importance of such a conversion was proved by the oxidation of the silicon surface,²⁷ phosphorene,²⁸ and freestanding δ_6 -borophene.²⁴

Surface oxidation may lead to the degradation of borophenes like black phosphorenes²⁹ and limit its applications. However, for the most important phase of borophenes on Ag(111) substrate, β_{12} -borophene (about 90% in ratio³⁰), there is a contradiction from experiments whether boron atoms in borophenes are active or inert to oxidation. Consequently, the oxidation mechanism of supported β_{12} -borophenes (e.g., role of triplet-to-singlet conversion) still remains basically unknown in both experiments and theory. In this study, we considered the adsorption and diffusion of oxygen atoms at first and then investigated the chemisorption and dissociation process of O₂ molecules; at last, calculated atomic core-level (CL) binding energies and experimental X-ray photoelectron spectroscopy were compared to resolve the contradiction from experiments.

METHODS

All the calculations were performed within the framework of plane-wave density functional theory (DFT), implemented in the Vienna *ab initio* simulation package (VASP).^{31,32} The projector augmented wave (PAW) pseudopotential method^{33,34} and Perdew-Burke-Ernzerhof (PBE) exchange-correlation functional³⁵ were selected. The atomic positions were optimized by using the conjugate gradient method until the Hellmann-Feynman force acting on each atom was smaller than 0.01 eV/Å. The kinetic energy cutoff for plane waves was set to 500 eV. A large vacuum spacing (>15 Å) was taken to prevent mirror interactions. The Brillouin zones were sampled with 0.096 $Å^{-1}$ spacing in reciprocal space by the Monkhorst-Pack scheme.³⁶ We selected 2 \times 2 and 2 \times 4 supercells of β_{12} -borophene on Ag(111) substrate as basic models for atomic and molecular oxygen adsorption, respectively. The Ag(111) substrate was modeled by a three-layer slab with only the bottom layer fixed. The crystal orbital Hamilton populations (COHP) analyses were performed by the LOBSTER program³⁷ for bonding analysis. Grimme's DFT-D3 van der Waals (vdW) corrections with the Becke–Johnson (BJ) damping^{38,39} was employed. The atomic core-level (CL) binding energies were evaluated by using the Janak-Slater (JS) transition state approach where half electron was shifted from the core state to the valence state,⁴⁰ given that this approach performs better than initial state and final state approaches.⁴¹ The climbing image nudged elastic band (CI-NEB) method 42,43 was used to search transition states with a force convergence criteria of 0.02 eV $Å^{-1}$.

We studied the adsorption energies of oxygen atoms and molecules on β_{12} -borophene supported by the Ag(111) substrate, which was the most preferred borophene on silver substrate.^{30,44,45} The average adsorption energy ($E_{\rm ad}$) was defined as follows:²⁸

$$E_{\rm ad} = (N_{\rm O}E_{\rm O_2}/2 + E_{\rm borophene} - E_{\rm total})/N_{\rm O}$$

where E_{O_2} , $E_{\text{borophene}}$, and E_{total} represent the energies of a triplet O_2 molecule in a vacuum, β_{12} -borophene supported on a silver substrate, and the total system with oxygen, respectively, and N_O is the number of oxygen atoms in each unit cell. In total, we considered 5 top sites (T), 8 bridge sites (BR), and 4 hollow sites (H) for the adsorption of an oxygen atom or molecule (as shown in Figure 1a), which was more complicated than the freestanding case due to the presence of the substrate.



Figure 1. (a) Illustration for different adsorption sites for oxygen atoms and molecules. Best adsorption site for an oxygen atom: (b) BR₁ and (c) BR₂. (d) Four typical diffusion paths of an O atom on supported β_{12} borophene and (e) energy evolution along corresponding paths. Pink, red, and gray balls stand for boron, oxygen, and silver atoms, respectively. Top (T), bridge (BR), and hollow (H) sites are represented by black triangles, blue circles, and red pentagrams, respectively. Diffusion barriers (eV) for rate-determining steps are labeled in the corresponding colors.

An triplet oxygen atom or molecule was initially placed at a height of about 2.1 Å above each adsorption site to find the best chemisorption sites, where total magnetization was variable. Two orientations (i.e., vertical abbreviated to "v" and horizontal abbreviated to "h") were taken into account for the initial O₂ molecules. According to the Bell–Evans–Polanyi (BEP) principle, the barrier difference is approximately proportional to the energy difference between the final state and the initial state, so the most stable chemisorption site for O₂ molecule and atom were selected for the study of oxidation process. In this process, the triplet O₂ molecules were optimized with fixed magnetization, while singlet states were optimized as closed-shell systems to avoid spin contamination.⁴⁶

RESULTS AND DISCUSSION

Whether the adsorption of oxygen atoms is exothermal or endothermal compared to triplet O₂ molecule is crucial for the oxidation process. The adsorption energies (at the PBE+D3 level) of oxygen atoms at different sites are listed in Table S1. It showed that an oxygen atom at the bridge sites BR_1 (E_{ad} = 2.561 eV) and BR₂ (E_{ad} = 2.322 eV) were much more stable than those at other sites, and they are a little larger than those on phospherene ($\leq 2.08 \text{ eV}^{28}$). In other words, an oxygen atom tends to bind to two boron atoms with lower coordination numbers (i.e., 4 or 5 as shown in Figure 1b,c). The BR_1 site was also be favored by oxygen atom on χ_3 -borophene supported by the Ag(111) substrate because of their geometrical similarity.²⁶ As seen above, the adsorption of oxygen atoms on β_{12} borophene was exothermal, and it released energies of >2.0 eV at preferred sites compared to the triplet O₂ molecule, which were even larger compared to a single oxygen atom in a vacuum (>5.0 eV).

In the case of BR_1 site (i.e., junction of two neighboring hexagonal boron rings), the oxygen atom gained about 1.55 e,

while adjacent boron atoms lost about 0.79 e from Bader charge analysis. The distance between the two boron atoms bonded to the oxygen atom was prolonged to 1.98 Å from 1.65 Å after adsorption, implying a break of the B–B bond and formation of B–O bonds. The bonding break and formation could be demonstrated by the charge density difference (CDD) and crystal orbital Hamilton populations (COHP) analysis. The CDD is calculated as

$$\Delta \rho = \rho_{\rm total} - \rho_{\rm borophene} - \rho_{\rm O_N}$$

where ρ_{O_N} (N = 1 or 2), $\rho_{\text{boropheney}}$ and ρ_{total} represent the electron densities of the oxygen atom or molecule in a vacuum, the borophene supported on silver, and the total system with oxygen adatoms, respectively. As shown in Figure S1, the CDD plot and close integrated COHP (iCOHP) values (i.e., 8.81 vs 8.91) indicated that two B–O bonds exhibited similar bonding behavior and very close bonding strength. The iCOHP value between the two boron atoms connected to the oxygen atom decreased to 1.65 from 5.25, which indicated that the B–O bonds drained most of the electrons between them, in accordance with the CDD plot.

Besides the adsorption energy, the migration of dissociated oxygen atoms on borophene is also very important in the oxidation process. Four typical complete diffusion paths (A, B, C, and D) are displayed in Figure 1d, and the relative energies and corresponding diffusion barriers ($\Delta E_{\rm b}$) for each step are plotted in Figure 1e. Paths A and B show that the diffusion across the center or along the edges of hexagonal holes was very difficult, which had high barriers of 3.91 or 1.78 eV at the ratedetermining steps, respectively. Path C shows that the diffusion of oxygen atoms from the site between hexagonal holes (i.e., BR_1) to filled-hexagon ribbon was difficult (with a barrier of 1.76 eV), and the reverse process was also difficult (with a barrier of 1.07 eV). In contrast, the diffusion across triangles (path D) was very easy, the highest barrier for which was only 0.30 eV, much lower than those for an oxygen atom on freestanding graphene (1.05 eV),⁴⁷ Ag-supported graphene (0.67 eV),⁴⁷ and supported χ_3 -borophene (0.76–0.98 eV).²⁶ According to the diffusion constants (D) expressed by the Arrhenius formula $D \propto$ $\exp(-\Delta E_{\rm b}/k_{\rm B}T)$, the diffusion of oxygen atoms on supported β_{12} -borophene would be much faster than those on freestanding graphene, Ag-supported graphene, and supported χ_3 -borophene. In a word, oxygen atoms between hexagonal holes tended to be pinned, while oxygen atoms on the filled-hexagon ribbons were prone to be mobile but confined on the ribbons.

Then we focused on the adsorption of O2 molecules. As mentioned above, triplet O2 molecules were initially placed at a height of about 2.1 Å above each adsorption site, where the height was defined as the distance from the basal plane of borophene to the center of a horizontal O2 molecule or the lower atom in a vertical molecule. After optimization with variable total magnetization, the corresponding average adsorption energies are listed in Table S2. For the adsorption of horizontal O_2 molecules, both two oxygen atoms were bonded to borophene in most cases ($E_{ad} = 0.65 - 1.03 \text{ eV}$), while one-end chemisorption ($E_{ad} = 0.11 - 0.42$ eV) or physisorption ($E_{ad} =$ 0.06-0.08 eV) was preferred for the vertical O₂ molecules. It indicated chemisorption preferred in most cases and high sensitivity to the initial position and orientation of O₂ molecules. As shown in Table S2 and Figure 2a-c, the O_2 molecules favored O_2-T_{3-h} and O_2-BR_{7-h} sites ($E_{ad} = 1.03$ and 1.00 eV, respectively), and the O_2-H_{1-h} site was also shown ($E_{ad} = 0.77$

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Figure 2. Preferred adsorption sites for an O₂ molecule on supported β_{12} -borophene: (a) O₂-T_{3-h}, (b) O₂-BR_{7-h}, (c) O₂-H_{1-h}, and corresponding configurations with two O₂ molecules dissociated: (d) 4O-T_{3-h}, (e) 4O-BR_{7-h}, and (f) 4O-H_{1-h}. Cyan and blue balls stand for boron atoms for core-level shifts calculations to compare with XPS.

eV), given that it corresponded to the most stable site for atom adsorption. Obviously, their adsorption energies were still very significant after compensation for the dissociation energy of an O_2 molecule.

Interestingly, 5 of 17 horizontal cases preferred the O_2-T_{3-h} configuration, which was also favored by supported δ_6 -borophene.²⁵ In details (as shown in Figure 2a), the O_2 molecule pulled two hexacoordinated boron atoms out of the basal plane and formed two B–O bonds (about 1.46 Å), with the cost of elongation of the O–O bond to 1.50 Å from 1.23 Å. The boron atoms bonded to oxygen atoms lost about 1.08 *e*, while oxygen atoms gained about 0.67/0.78 *e* from Bader charge analysis. The iCOHP values for the two B–O bonds were 9.06, which implied a little stronger bonds than those in the case of atom adsorption (about 8.8 for the BR₁ site). The lengths and iCOHP values of B–O bonds for the O_2 –BR_{7-h} site (Figure 2b) were 1.44/1.48 Å and 9.03/8.16, respectively, and the corresponding values for the O_2 –H_{1-h} site were 1.47 Å and 8.41 (Figure 2c). The short and strong B–O bonds would benefit the dissociation of O_2 molecules.

The kinetic processes of adsorption and dissociation of O_2 molecule at O_2-T_{3-h} and O_2-H_{1-h} sites were investigated by the CI-NEB method (as shown Figure 3a,b). The supported borophene may be oxidized by a direct process or an indirect process like the oxidation of phospherene.²⁸ However, we found



Figure 3. Energy profiles of adsorption and dissociation of O₂ against the average height of two O atoms above the supported borophene for (a) O_2-T_{3-h} and (b) O_2-H_{1-h} sites. The solid (dotted) lines indicate the PESs calculated with fixed (variable) total magnetization. S and T stand for singlet and triplet states, respectively. Barriers (eV) for adsorption and dissociation are labeled in corresponding colors.

that the chemisorption state of O_2 molecule appeared as intermediate in the calculation of the direct process, so only the indirect process was studied. For the $O_2 - T_{3-h}$ site, the triplet O_2 molecule was initially physisorbed at a height of about 3.02 Å parallel to the supported borophene with very small adsorption energy. When the O_2 molecule gets close to the borophene, the singlet state would become more stable due to the hybridization between $O_2 \pi_{2p}^*$ orbitals and the substrate atoms (i.e., a chemisorption state). A spin-unrestricted variable-magnetization calculation gave a barrier of 0.07 eV to separate the physisorbed triplet O₂ and chemisorbed singlet configuration, while the barrier increased to 0.09 eV when triplet state was fixed. A very small triplet-to-singlet conversion barrier (i.e., 0.05 eV) was observed, in accordance with a previous study that the δ_6 -borophene lost spin triplet-to-singlet conversion upon the presence of the Ag(111) substrate.²⁵ The adsorption of singlet O2 molecules tends to be a barrierless process, and the barrier from physisorption to chemisorption for triplet O₂ molecules may be easily overcome by their kinetic energies. It is different from the adsorption of O_2 on Ag-supported graphene, which has stable physisorption configurations.

It should be noted that for the saddle-point geometry the presence of silver substrate makes more electrons (about 0.19 e from Bader charge analysis) transfer to the O₂ molecule, while more spin (about 0.016 e) distributed on the borophene and substrate compared to the case without silver substrate in the fixed triplet-state calculation. As a result, the total energy of the triplet-state system decreased rather than increased when getting close to the borophene, similar to the adsorption of triplet O_2 molecule on Si(100) surface.⁴⁸ The chemisorption barrier was also very low for the $O_2 - H_{1-h}$ site (i.e., 0.07 eV), and spin triplet-to-singlet conversion was not observed. In other words, the silver substrate enhanced the reducibility of the borophene, which led to the initial chemisorption of O₂ molecules being very easy and the triplet-to-singlet conversion being not important, quite different from its important role in the oxidation of phosphorenes.²⁸

The stabilities of the adsorbed molecules could be evaluated by their lifetimes. According to the canonical transition-state theory (CTST), the lifetime (τ) of adsorbed O₂ molecules could be roughly estimated by the following formula:⁴⁹

$$\tau = \frac{h \ln 2}{k_{\rm B}T} \exp\left(\frac{\Delta E_{\rm b}'}{k_{\rm B}T}\right)$$

where h, $k_{\rm B}$, T, and $\Delta E'_{\rm b}$ are Planck's constant, Boltzmann's constant, temperature, and dissociation barrier, respectively. As a result, O_2 molecules at O_2-T_{3-h} and O_2-H_{1-h} sites would dissociate by overcoming very small barriers ($\Delta E_{\rm b}^{\prime}$) of 0.12 and 0.19 eV (as shown in Figure 3a,b), which correspond to 0.56 and 2.19 ps, respectively, at 600 K, the typical temperature of synthesizing borophene on the silver substrate. The corresponding lifetimes increased to 11.50 and 172.48 ps at room temperature (300 K). The corresponding average adsorption energies increased to 1.62 and 2.63 eV after dissociation, indicating exothermic reactions with significant energy release (i.e., 0.61 and 1.86 eV per O atom, respectively). The dissociated oxygen atoms at the $2O-T_{3-h}$ site are likely to diffuse to other sites due to the low diffusion barriers for an oxygen atom along the filled-hexagon ribbons. It may imply a most preferred path for O_2 molecule dissociation. In the meanwhile, some dissociated oxygen atoms were pinned at the BR1 site as in the cases of 2O-BR_{7-h} and 2O-H_{1-h} sites.

Given all that, the O_2 molecules tend to be easily chemisorbed on supported β_{12} -borophene and dissociate into separated atoms by overcoming very low barriers. However, why is the ratio of oxidized to unoxidized boron atoms in borophene from XPS so small (about 0.23)?¹² We tried to uncover the states of oxidized borophene in experiments by comparing simulated core-level binding energies with XPS, which reflected the charge states of elements in terms of the chemical shift.

In the Janak–Slater (JS) transition state approach,⁴⁰ the evaluation at midpoint was used to calculate core-level shifts (CLSs) as follows:

$$E_{\text{CLS}}^{\text{JS}} = -\Delta\varepsilon_i = -\varepsilon_i(1/2) + \varepsilon_i^{\text{ref}}(1/2)$$

where the core-level eigenvalues ε_i are given with the Fermi level set as zero.⁵⁰ It should be noted that the binding energies predicted by VASP/PAW do not directly match experimental core-level binding energies due to nonexplicit accounting for core electron energies; however, the calculated relative binding energy shifts line up well with experimental trends.⁴¹ To check the reliability of such a method, three nonequivalent boron atoms (cyan balls in Figure 2) far from oxygen atoms were examined, where the tetra-coordinated one was selected as the reference (ref). Then the binding energies for B 1s levels of nonequivalent boron atoms (blue balls in Figure 2) around oxygen atoms (red balls in Figure 2) were calculated, and the simulated core-level binding energy for the reference boron atom (ref) was shifted to the corresponding experimental value.³⁰

The simulated core-level shifts for bared β_{12} -borophene supported on an Ag(111) substrate were examined (as shown in Figure 4a), which showed very small deviations (<0.15 eV) for the peak positions compared to experimental XPS.³⁰ In the case of oxidized borophene, the simulated core-level binding energies (filled cyan curves in Figure 4b–j) for the boron atoms (cyan balls in Figure 2) far from oxygen atoms were very close to those in bared borophene, which suggested the reliability of the corelevel shift simulations for boron atoms. As shown in Figure 4b– g, for the three selected sites (i.e., T_{3-b}, BR_{7-b}, and H_{1-h}), there were binding energy peaks near two experimental peak positions (i.e., 187.1 and 188.2 eV¹²), regardless of whether or not the O₂ molecule dissociated. However, none of the six structures could account for the highest XPS peak position located at 191.5 eV¹² (as shown in Figure 4b–g).

Considering that the binding energy of the B 1s orbital in bulk B_2O_3 is about 190.5 eV,⁵¹ a boron atom coordinated with more oxygen atoms may account for the highest peak position. So another O₂ molecule was adsorbed on the 2O-T_{3-b}, 2O-BR_{7-b}, and 2O-H_{1-h} structures, and the corresponding structures with two O2 molecules dissociated (i.e., 40-T3-h, 40-BR7-h, and $4O-H_{1-h}$) are displayed in Figure 2d-f. The simulated corelevel binding energies for 4O-T_{3-h}, 4O-BR_{7-h}, and 4O-H_{1-h} structures are displayed in Figure 4h-j, and each peak was labeled with n:m, which stands for a boron atom coordinated with *n* boron and *m* oxygen atoms. It showed that boron atoms coordinated with three oxygen atoms (labeled with 0:3) basically located near the highest XPS peak position, while the lowest XPS peak position corresponded to boron atoms coordinated with only boron atoms (labeled with 3:0, 4:0, or 5:0). It was in agreement with the assumption by Feng et al. for these two peaks in the XPS experiment.¹²

Interestingly, as shown in Figure 4b—j, there were some boron atoms coordinated with both oxygen and boron atoms, the corelevel binding energies for which located near the middle peak



Figure 4. Simulated core-level binding energies for (a) bared β_{12} borophene supported on Ag (111), (b–d) supported β_{12} -borophene with an O₂ molecule, (e–g) supported β_{12} -borophene with an O₂ molecule dissociated, and (h–j) supported β_{12} -borophene with two O₂ molecules dissociated. *n*:*m* labeled near peaks stands for a boron atom coordinated with *n* boron and *m* oxygen atoms. Exp. 1 and 2 represent the corresponding experimental XPS peak positions for bared and oxidized supported borophenes, respectively.^{12,30}

position of the XPS experiment.¹² It seemed to deny the simple assumption by Feng et al. that it came from boron atoms coordinated with only boron atoms (i.e., unoxidized boron).¹² As a result, the measured area ratio (about 0.23) of oxidized to unoxidized boron based on the assumption above may be greatly underestimated, and there should be more partially oxidized boron atoms. It agreed to the foregoing conclusion that the O₂ molecules chemisorbed and dissociated easily on supported β_{12} -borophene, which led to oxidation of many boron atoms.

On the basis of the analyses above, we proposed a novel B_5O_4 sheet (as shown in Figure 5a,b), derived from the pristine β_{12} borophene unit cell on the Ag (111) substrate with two O_2 molecules dissociated, though it was stable only at low temperatures (e.g., 200 K from Born–Oppenheimer molecular dynamics simulations). The coordination numbers and shifted core-level binding energies for all boron atoms in the supported B_5O_4 sheet are shown in Figure 5c, which indicated that the sheet accounted for the three XPS peak positions well. It further suggested that the middle peak may be contributed by boron atoms coordinated with both boron and oxygen atoms; in other words, most of the boron atoms in the borophene were oxidized. It indicated that boron atoms inside borophene islands would be active rather than inert to oxidation, which was very important for its further applications. pubs.acs.org/JPCC



Figure 5. (a) Top and (b) side views of supported B_5O_4 sheet, (c) shifted core-level binding energies for supported B_5O_4 sheet broadened with different full width at half-maximum (i.e., FWHM = 1.0 and 1.5 eV), (d) projected band structure of the supported B_5O_4 sheet (inset is first Brillouin zone), and (e) energy surfaces in area A. The XPS peaks come from experimental results for oxidized supported borophene.¹²

The projected band structure of supported B_5O_4 sheet was calculated. As shown in Figure 5d, some bands with contributions of boron atoms were crossed by the Fermi level, which indicated that the B_5O_4 sheet was metallic in nature. The bands contributed by oxygen atoms were much lower than the Fermi level, which came from strong covalent B–O bonds. Thus, the metallicity of the B_5O_4 sheet was derived from the delocalized bonding among boron atoms clinging to the silver surface, which could be confirmed by the electron localization function (ELF) plot (as shown in Figure S2a). Interestingly, there appears to be a gapped Dirac cone in area A (marked in Figure 5d), the gap for which is about 0.05 eV. However, the energy surfaces in area A (displayed in Figure 52b from different views) suggested two bottom-to-bottom valleys, which may lead to significant anisotropy in transport properties.

In consideration of the oxidation activity of β_{12} -borophenes, constructing sandwich or layered heterogeneous structures may be a good way for protection.⁵² Free-standing β_{12} -borophenes sandwiched by graphenes and BN monolayers are shown in Figure S3a,b. The mismatch in two structures was close to or smaller than 1%, and the distances between layers was about 3.5 Å after optimization, a typical distance of van der Waals interaction. It implied that the structures and properties of borophenes would be maintained with the protection of graphenes or BN monolayers.

CONCLUSIONS

We have systematically investigated the adsorption, diffusion, or dissociation of oxygen atoms and molecules on β_{12} borophene supported on a Ag(111) substrate using DFT methods. The O_2 molecules tend to be chemisorbed on supported β_{12} borophene easily and dissociate into separated atoms by overcoming very low barriers. The spin triplet-to-singlet conversion is not important in the chemisorption process because of the enhanced reducibility of the borophene upon the presence of the silver substrate. It is found that O₂ molecules prefer to be adsorbed on two hexacoordinated boron atoms, which tend to dissociate and diffuse along filled-hexagon ribbons, while some oxygen atoms are pinned between hexagonal holes. A comparison between our calculated core-level binding energies and the experimental Xray photoelectron spectroscopy, in combination with detailed kinetic analyses, indicates that boron atoms in supported borophenes are active rather than inert to oxidation. Furthermore, we proposed a model B_5O_4 sheet with most boron atoms oxidized, which accounted for the three XPS peak positions well and further confirmed the oxidation activity of supported borophenes. It should be noted that our results also suggest that the middle one of the three typical XPS peaks for boron nanostructures may come from partially oxidized boron, which was regarded as a fingerprint for unoxidized boron atoms in some previous studies. In a word, the results on the oxidation stability and mechanism of supported borophenes resolved the contradiction from experiments whether boron atoms in supported borophenes were active or inert to oxidation, which suggests the protection of borophenes from oxygen (e.g., constructing sandwich or layered heterogeneous structures) is therefore essential for their broad applications.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.jpcc.0c09297.

Adsorption energies for oxygen atoms and molecules on supported β_{12} -borophene, charge density difference for the borophene with an oxygen adatom, crystal orbital Hamilton population (COHP) curves for B–O and B–O bonds, electron localization function for supported B₅O₄ sheet and optimized β_{12} borophenes sandwiched by graphenes and BN monolayers (PDF)

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Notes

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REFERENCES

(1) Zhang, Y.; Tan, Y.-W.; Stormer, H. L.; Kim, P. Experimental observation of the quantum Hall effect and Berryas phase in graphene. *Nature* **2005**, *438*, 201–204.

(2) Williams, J. R.; DiCarlo, L.; Marcus, C. M. Quantum Hall effect in a gate-controlled p-n junction of graphene. *Science* **2007**, *317*, 638-641.

(3) Morozov, S. V.; Novoselov, K. S.; Katsnelson, M. I.; Schedin, F.; Elias, D. C.; Jaszczak, J. A.; Geim, A. K. Giant intrinsic carrier mobilities in graphene and its bilayer. *Phys. Rev. Lett.* **2008**, *100*, 016602.

(4) Jin, C.; Lin, F.; Suenaga, K.; Iijima, S. Fabrication of a freestanding boron nitride single layer and its defect assignments. *Phys. Rev. Lett.* **2009**, *102*, 195505.

(5) Lalmi, B.; Oughaddou, H.; Enriquez, H.; Kara, A.; Vizzini, S.; Ealet, B.; Aufray, B. Epitaxial growth of a silicene sheet. *Appl. Phys. Lett.* **2010**, *97*, 223109.

(6) Tang, H.; Ismail-Beigi, S. Novel Precursors for Boron Nanotubes: The Competition of Two-Center and Three-Center Bonding in Boron Sheets. *Phys. Rev. Lett.* **2007**, *99*, 115501.

(7) Zhang, Z.; Mannix, A. J.; Liu, X.; Hu, Z.; Guisinger, N. P.; Hersam, M. C.; Yakobson, B. I. Near-equilibrium growth from borophene edges on silver. *Sci. Adv.* **2019**, *5*, eaax0246.

(8) Piazza, Z. A.; Hu, H. S.; Li, W. L.; Zhao, Y. F.; Li, J.; Wang, L. S. Planar Hexagonal B₃₆ as a Potential Basis for Extended Single-atom Layer Boron Sheets. *Nat. Commun.* **2014**, *5*, 3113.

(9) Mu, Y.; Chen, Q.; Chen, N.; Lu, H.-G.; Li, S.-D. A novel borophene featuring heptagonal holes: a common precursor of borospherenes. *Phys. Chem. Chem. Phys.* **2017**, *19*, 19890–19895.

(10) Penev, E. S.; Bhowmick, S.; Sadrzadeh, A.; Yakobson, B. I. Polymorphism of Two-Dimensional Boron. *Nano Lett.* **2012**, *12*, 2441–2445.

(11) Mannix, A. J.; Zhou, X.-F.; Kiraly, B.; Wood, J. D.; Alducin, D.; Myers, B. D.; Liu, X.; Fisher, B. L.; Santiago, U.; Guest, J. R.; et al. Synthesis of borophenes: Anisotropic, two-dimensional boron polymorphs. *Science* **2015**, *350*, 1513–1516.

(12) Feng, B.; Zhang, J.; Zhong, Q.; Li, W.; Li, S.; Li, H.; Cheng, P.; Meng, S.; Chen, L.; Wu, K. Experimental realization of two-dimensional boron sheets. *Nat. Chem.* **2016**, *8*, 563–568.

(13) Li, W.; Kong, L.; Chen, C.; Gou, J.; Sheng, S.; Zhang, W.; Li, H.; Chen, L.; Cheng, P.; Wu, K. Experimental realization of honeycomb borophene. *Sci. Bull.* **2018**, *63*, 282–286.

(14) Wu, R.; Drozdov, I. K.; Eltinge, S.; Zahl, P.; Ismail-Beigi, S.; Božović, I.; Gozar, A. Large-area single-crystal sheets of borophene on Cu(111) surfaces. *Nat. Nanotechnol.* **2019**, *14*, 44–49.

(15) Zhang, X.; Hu, J.; Cheng, Y.; Yang, H. Y.; Yao, Y.; Yang, S. A. Borophene as an extremely high capacity electrode material for Li-ion and Na-ion batteries. *Nanoscale* **2016**, *8*, 15340–15347.

(16) Wang, H.; Li, Q.; Gao, Y.; Miao, F.; Zhou, X.-F.; Wan, X. G. Strain effects on borophene: ideal strength, negative Possion's ratio and phonon instability. *New J. Phys.* **2016**, *18*, 073016.

(17) Mortazavi, B.; Rahaman, O.; Dianat, A.; Rabczuk, T. Mechanical responses of borophene sheets: a first-principles study. *Phys. Chem. Chem. Phys.* **2016**, *18*, 27405–27413.

(18) Zhang, Z.; Yang, Y.; Penev, E. S.; Yakobson, B. I. Elasticity, Flexibility and Ideal Strength of Borophenes. *Adv. Funct. Mater.* **2017**, 27, 1605059.

(19) Ling, C.; Shi, L.; Ouyang, Y.; Zeng, X. C.; Wang, J. Nanosheet Supported Single-Metal Atom Bifunctional Catalyst for Overall Water Splitting. *Nano Lett.* **2017**, *17*, 5133–5139.

(20) Wang, Y.; Mu, Y.; Li, S.-D. Exfoliation of Borophenes from Silver Substrates Assisted by Li/Mg Atoms—a Density Functional Theory Study. J. Mater. Chem. C 2019, 7, 4043–4048.

(21) Aji, L. B. B.; Baker, A. A.; Bae, J. H.; Hiszpanski, A. M.; Stavrou, E.; McCall, S. K.; Kucheyev, S. O. Degradation of ultra-thin boron films in air. *Appl. Surf. Sci.* **2018**, *448*, 498–501.

(22) He, Y.; Cheng, N.; Chen, C.; Xiong, S.; Zhao, J. Tuning the electronic transport anisotropy in borophene via oxidation strategy. *Sci. China: Technol. Sci.* **2019**, *62*, 799–810.

(23) Lherbier, A.; Botello-Méndez, A. R.; Charlier, J.-C. Electronic and optical properties of pristine and oxidized borophene. 2D Mater. 2016, 3, 045006.

(24) Guo, R.-Y.; Li, T.; Shi, S.-E.; Li, T.-H. Oxygen defects formation and optical identification in monolayer borophene. *Mater. Chem. Phys.* **2017**, *198*, 346–353.

(25) Alvarez-Quiceno, J. C.; Miwa, R. H.; Dalpian, G. M.; Fazzio, A. Oxidation of free-standing and supported borophene. 2D Mater. 2017, 4, 025025.

(26) Luo, W. W.; Liu, G.; Wang, X.; Lei, X. L.; Ouyang, C. Y.; Liu, S. Q. The adsorption and dissociation of oxygen on Ag (111) supported χ_3 borophene. *Phys. B* **2018**, *537*, 1–6.

(27) Kato, K.; Uda, T.; Terakura, K. Backbond Oxidation of the Si(001) Surface: Narrow Channel of Barrierless Oxidation. *Phys. Rev. Lett.* **1998**, *80*, 2000–2003.

(28) Ziletti, A.; Carvalho, A.; Campbell, D. h.; Coker, D. h.; Castro Neto, A. h. Oxygen Defects in Phosphorene. *Phys. Rev. Lett.* **2015**, *114*, 046801.

(29) Zhou, Q.; Chen, Q.; Tong, Y.; Wang, J. Light-Induced Ambient Degradation of Few-Layer Black Phosphorus: Mechanism and Protection. *Angew. Chem., Int. Ed.* **2016**, *55*, 11437–11441.

(30) Campbell, G. P.; Mannix, A. J.; Emery, J. D.; Lee, T.-L.; Guisinger, N. P.; Hersam, M. C.; Bedzyk, M. J. Resolving the Chemically Discrete Structure of Synthetic Borophene Polymorphs. *Nano Lett.* **2018**, *18*, 2816–2821.

(31) Kresse, G.; Furthmuller, J. Efficient iterative schemes for ab initio total-energy calculations using a plane-wave basis set. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1996**, *54*, 11169–11186.

(32) Kresse, G.; Hafner, J. Norm-conserving and ultrasoft pseudopotentials for first-row and transition elements. *J. Phys.: Condens. Matter* **1994**, *6*, 8245–8257.

(33) Blochl, P. E. Projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1994**, *50*, 17953–17979.

(34) Kresse, G.; Joubert, D. From ultrasoft pseudopotentials to the projector augmented-wave method. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1999**, *59*, 1758–1775.

(35) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized gradient approximation made simple. *Phys. Rev. Lett.* **1996**, 77, 3865–3868.

(36) Monkhorst, H. J.; Pack, J. D. Special points for Brillouin-zone integrations. *Phys. Rev. B* **1976**, *13*, 5188–5192.

(37) Maintz, S.; Deringer, V. L.; Tchougréeff, A. L.; Dronskowski, R. LOBSTER: A tool to extract chemical bonding from plane-wave based DFT. *J. Comput. Chem.* **2016**, *37*, 1030–1035.

(38) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. A consistent and accurate ab initio parametrization of density functional dispersion correction (DFT-D) for the 94 elements H-Pu. *J. Chem. Phys.* **2010**, *132*, 154104.

(39) Grimme, S.; Ehrlich, S.; Goerigk, L. Effect of the damping function in dispersion corrected density functional theory. *J. Comput. Chem.* **2011**, *32*, 1456–1465.

(40) Köhler, L.; Kresse, G. Density functional study of CO on Rh(111). *Phys. Rev. B: Condens. Matter Mater. Phys.* **2004**, *70*, 165405.

(41) Bellafont, N. P.; Viñes, F.; Hieringer, W.; Illas, F. Predicting core level binding energies shifts: Suitability of the projector augmented wave approach as implemented in VASP. *J. Comput. Chem.* **2017**, *38*, 518–522.

(42) Henkelman, G.; Uberuaga, B. P.; Jónsson, H. A climbing image nudged elastic band method for finding saddle points and minimum energy paths. J. Chem. Phys. **2000**, 113, 9901.

(43) Henkelman, G.; Jónsson, H. Improved tangent estimate in the nudged elastic band method for finding minimum energy paths and saddle points. *J. Chem. Phys.* **2000**, *113*, 9978.

(44) Zhang, Z.; Yang, Y.; Gao, G.; Yakobson, B. I. Two-Dimensional Boron Monolayers Mediated by Metal Substrates. *Angew. Chem., Int. Ed.* **2015**, *54*, 13022–13026.

(45) Shu, H.; Li, F.; Liang, P.; Chen, X. Unveiling the atomic structure and electronic properties of atomically thin boron sheets on an Ag(111) surface. *Nanoscale* **2016**, *8*, 16284–16291.

(46) Chan, S.-P.; Chen, G.; Gong, X. G.; Liu, Z.-F. Oxidation of Carbon Nanotubes by Singlet O₂. *Phys. Rev. Lett.* **2003**, *90*, 086403.

(47) Zhang, Z.; Yin, J.; Liu, X.; Li, J.; Zhang, J.; Guo, W. Substrate-Sensitive Graphene Oxidation. *J. Phys. Chem. Lett.* **2016**, *7*, 867–873.

(48) Fan, X. L.; Zhang, Y. F.; Lau, W. M.; Liu, Z. F. Adsorption of Triplet O_2 on Si(100): The Crucial Step in the Initial Oxidation of a Silicon Surface. *Phys. Rev. Lett.* **2005**, *94*, 016101.

(49) Bozkaya, U.; Turney, J. M.; Yamaguchi, Y.; Schaefer, H. F. The barrier height, unimolecular rate constant, and lifetime for the dissociation of HN_2 . J. Chem. Phys. **2010**, 132, 064308.

(50) Olovsson, W.; Göransson, C.; Pourovskii, L. V.; Johansson, B.; Abrikosov, I. A. Core-level shifts in fcc random alloys: A first-principles approach. *Phys. Rev. B: Condens. Matter Mater. Phys.* **2005**, *72*, 064203.

(51) Ong, C. W.; Huang, H.; Zheng, B.; Kwok, R. W. M.; Hui, Y. Y.; Lau, W. M. X-ray photoemission spectroscopy of nonmetallic materials: Electronic structures of boron and B_xO_y . J. Appl. Phys. **2004**, 95, 3527–3534.

(52) Zhang, Z.; Penev, E. S.; Yakobson, B. I. Two-dimensional boron: structures, properties and applications. *Chem. Soc. Rev.* **201**7, *46*, 6746–6763.