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

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Abstract

Oxidation stability of borophene is deemed as a prerequisite for its broad applications, however there is a contradiction from experiments whether boron atoms in borophenes are active or inert to oxidation. Our detailed density functional theory calculations performed herein indicate that O_2 molecules tend to be chemisorbed on supported β_{12} borophene easily and dissociate into separated atoms by overcoming very low barriers, and spin tripletto-singlet conversion is not important in the chemisorption process. It is found that O_2 molecules prefer to be adsorbed on two hexacoordinated boron atoms, 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 chemi-

cal 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 monolayer⁴, silicon monolayer⁵ and boron monolayer 6,7 (referred to as borophene⁸). Due to multi-center 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 Since the successful synthesis of realized. 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 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 negative Possion's ratio¹⁶⁻¹⁸. Isolated nickel atoms supported on β_{12} borophene were predicted to be single-atom bifunctional catalyst for overall water splitting¹⁹.

As the prerequisites for the broad applications of borophenes, besides exfoliation²⁰, 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, and 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 layer¹¹. It was also reported that boron films with thicknesses of < 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 conversion²⁴. Another group drew a similar conclusion for freestanding δ_6 borophene, but the spin triplet-tosinglet conversion was not observed upon the presence of Ag(111) substrate²⁵, however, how the triplet O_2 molecule converted to singlet state when getting close to the substrate maintained unclear. Another study investigated the oxidation of supported χ_3 borophene, but the study neglected the spin triplet-to-singlet conversion²⁶, while the importance of such conversion was proved by the oxidation of silicon surface²⁷, phosphorene²⁸ and freestanding δ_6 borophene²⁴.

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. And 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, then investigated the chemisorption and dissociation process of O_2 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 carried out within the framework of plane-wave density functional theory (DFT), implemented in 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 using 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 (more than 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 scheme³⁶. A 2 × 2 and 2 × 4 supercells of β_{12} borophene on Ag(111) substrate were selected as basic model for atomic and molecular oxygen adsorption, respectively. The Ag(111) substrate was modeled by a three-layer slab with only bottom layer fixed. The crystal orbital Hamilton populations (COHP) analyses were performed by LOBSTER program³⁷ for bonding analysis. Grimme's DFT-D3 van der Waals (vdW) corrections with the Becke-Jonson (BJ) damping^{38,39} was employed. The atomic corelevel (CL) binding energies were evaluated using Janak–Slater (JS) transition state approach where half electron was shifted from the core state to the valence state⁴⁰, given that this approach performs better than initial state and final state approaches⁴¹. The climbing image nudged elastic band (CI-NEB) method^{42,43} was used to search transition states with a force convergence criteria of $0.02 \text{ eV}\text{Å}^{-1}$.

We studied the adsorption energies of oxygen atoms and molecules on β_{12} borophene supported by Ag(111) substrate, which was the most preferred borophene on silver substrate^{30,44,45}. The average adsorption energies $(E_{\rm ad})$ was defined as follows²⁸:

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

where E_{O_2} , $E_{Borophene}$ and E_{total} stood for the energies of an triplet O_2 molecule in vacuum, β_{12} borophene supported on silver substrate and the total system with oxygen, respectively, and N_O was the number of oxygen atoms in each unitcell. 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 Fig. 1a), which was more complicated than the freestanding case due to the presence of substrate.

An triplet oxygen atom or molecule was initially placed at a height of about 2.1 Å above each adsorption site to find 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 initial O_2 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 O_2 molecule and atom were selected for the study of oxidation process. In this process, the triplet O_2 molecules were optimized with fixed magnetization, while singlet states were optimized as closed-shell systems to avoid spin contamina $tion^{46}$.

Results & Discussion

Whether the adsorption of oxygen atoms are exothermal or endothermal compared to triplet O_2 molecule is crucial for the oxidation process. The adsorption energies (at PBE+D3 level) of oxygen atoms at different sites were listed in Table S1. It showed that an oxygen atom at the bridge sites BR₁ ($E_{ad} = 2.561 \text{ eV}$) and BR₂ ($E_{ad} = 2.322 \text{ eV}$) 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



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 grey 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 ratedetermining steps are labeled in corresponding colors.

other words, an oxygen atom tends to bind to two boron atoms with lower coordination numbers (i.e., 4 or 5 as shown in Fig. 1b,c). The BR₁ site was also be favored by oxygen atom on χ_3 borophene supported by Ag(111) substrate due to their geometrical similarity²⁶. As seen above, the adsorption of oxygen atoms on β_{12} borophene was exothermal, and it released energies of more than 2.0 eV at preferred sites compared to triplet O₂ molecule, which were even larger compared to single oxygen atom in 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 break of 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 was calculated as

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

, where ρ_{O_N} (N = 1 or 2), $\rho_{Borophene}$ and ρ_{total} stand for the electron densities of the oxygen atom or molecule in vacuum, the borophene supported on silver and the total system with oxygen adatoms, respectively. As shown in Fig. 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 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) were displayed in Fig. 1d, and the relative energies and corresponding diffusion barriers (ΔE_b) for each step were plotted in Fig. Paths A and B showed that the diffu-1e. sion 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 showed that the diffusion of oxygen atoms from the site between hexagonal holes (i.e., BR_1) to filledhexagon 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 $(1.05 \text{ eV})^{47}$, Agsupported graphene $(0.67 \text{ eV})^{47}$, and supported χ_3 borophene $(0.76 \sim 0.98 \text{ eV})^{26}$. According to the diffusion constants (D) expressed by the Arrhenius formula: $D \propto \exp(-\Delta E_b/k_B T)$, 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 pined, while oxygen atoms on the filled-hexagon ribbons were prone to be mobile but confined on the ribbons.



Figure 2: Preferred adsorption sites for an O_2 molecule on supported β_{12} borophene: (a) O_2 - T_{3-h} , (b) O_2 - BR_{7-h} , (c) O_2 - H_{1-h} , and corresponding configurations with two O_2 molecules dissociated: (d) 4O- T_{3-h} , (e) 4O- BR_{7-h} , (f) 4O- H_{1-h} . Cyan and blue balls stand for boron atoms for core-level shifts calculations to compare with XPS.

Then we focused on the adsorption of O_2 molecules. As mentioned above, triplet O_2 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 O_2 molecule or the lower atom in a vertical molecule. After optimization with variable total magnetization, the corresponding average adsorption energies were listed in Table S2. For the adsorption of horizontal O_2 molecules, both two oxygen atoms were bonded to borophene in most cases ($E_{\rm ad} = 0.65 \sim 1.03$ eV), while one-end chemisorption $(E_{\rm ad} = 0.11 \sim 0.42 \text{ eV})$ or physisorption $(E_{\rm ad} = 0.06 \sim 0.08 \text{ eV})$ were preferred for the vertical O_2 molecules. It indicated chemisorption preferred in most cases and high sensitivity to the initial position and orientation of O_2 molecules. As shown in Table S2 and Fig. 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 O_2 -H_{1-h} site was also shown $(E_{\rm ad} = 0.77 \text{ eV})$, 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 O_2 - T_{3-h} configuration , which was also favored by supported δ_6 borophene²⁵. In details (as shown in Fig. 2a), the O_2 molecule pulled two hexa-coordinated boron atoms out of the basal plane and formed two B-O bonds (about 1.46 Å), with the cost of elongation of 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~efrom 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 BR_1 site). The lengths and iCOHP values of B-O bonds for O_2 -BR_{7-h} site (Fig. 2b) were 1.44/1.48 Å and 9.03/8.16, respectively, and corresponding values for O_2 - H_{1-h} site were 1.47 Å and 8.41 (Fig. 2c). The short and strong B-O bonds would benefit to 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 CI-NEB method (as shown Fig. 3a-b). The supported borophene may be oxidized by a direct process or an indirect process like the oxidation of phospherene²⁸. However, we found that the chemisorption state of O_2 molecule appeared as intermediate in the calculation of direct process, so only the indirect process was studied. For 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, singlet state would become more stable due to the hybridization between $O_2 \pi^*_{2n}$ 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 O_2 and chemisorbed singlet configuration, while the barrier increased to 0.09 eV when triplet state was fixed. A very small tripletto-singlet conversion barrier (i.e., 0.05 eV) was observed, in accordance with a previous study



Figure 3: Energy profiles of adsorption and dissociation of O_2 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 δ_6 borophene lost spin triplet-to-singlet conversion upon the presence of Ag(111) substrate²⁵. The adsorption of singlet O₂ molecules tend to be a barrier-less 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 O₂ on Ag-supported graphene, which has stable physisorption configurations⁴⁷.

It should be noted that, for the saddlepoint geometry, the presence of silver substrate make 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 O₂ molecule on Si(100) surface⁴⁸. The chemisorption barrier was also very low for O₂- H_{1-h} site (i.e., 0.07 eV), and spin triplet-tosinglet conversion was not observed. In other words, the silver substrate enhanced the reducibility of the borophene, which led to that the initial chemisorption of O₂ molecules would be very easy and triplet-to-singlet conversion was not important, quite different from its important role in the oxidation of phosphorenes²⁸.

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 formula⁴⁹:

$$\tau = \frac{h \ln 2}{k_{\rm B}T} \exp(\frac{\Delta E_b'}{k_{\rm B}T})$$

where h, $k_{\rm B}$, T and $\Delta E'_b$ are Plank constant, Boltzmann 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 $(\Delta E'_{h})$ of 0.12 and 0.19 eV (as shown in Fig. 3a-b), which corresponded to 0.56 and 2.19 ps at 600 K, the typical temperature of synthesizing borophene on silver substrate, respectively. The corresponding lifetimes increased to 11.50 and 172.48 ps at room temperature of 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 $2O-T_{3-h}$ 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 BR_1 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 the ratio of oxidized to unoxidized boron atoms in borophene from XPS was 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 chemical shift.

In Janak–Slater (JS) transition state approach⁴⁰, the evaluation at midpoint was used to calculate core-level shifts (CLSs) as follows:

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

where the core-level eigenvalues ε_i are given with the Fermi level set as zero⁵⁰. 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 . In order to check the reliability of such method, three nonequivalent boron atoms (cyan balls in Fig. 2) far from oxygen atoms were examined, where the tetra-coordinated one was selected as reference (ref). Then the binding energies for B 1s levels of nonequivalent boron atoms (blue balls in Fig. 2) around oxygen atoms (red balls in Fig. 2) were calculated, and the simulated core-level binding energy for the reference boron atom (ref) was shifted to corresponding experimental value³⁰.

The simulated core-level shifts for bared β_{12} borophene supported on Ag(111) substrate were examined (as shown in Fig. 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 Fig. 4b-j) for the boron atoms (cyan balls in Fig. 2) far from oxygen atoms were very close to those in bared borophene, which suggested the reliability of the core-level shift simulations for boron atoms. As shown in Fig. 4b-g, for the three selected sites (i.e., T_{3-h} , BR_{7-h} 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 O_2 molecule dissociated. However, none of the 6 structures could account for the highest XPS peak position located at 191.5 eV^{12} (as shown in Fig. 4b-g).



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 corresponding experimental XPS peak positions for bared and oxidized supported borophenes, respectively^{12,30}.

Considering that the binding energy of the B 1s orbital in bulk B_2O_3 is about 190.5 eV⁵¹, an boron atom coordinated with more oxygen atoms may account for the highest peak position. So another O_2 molecule was adsorbed on the 2O-T_{3-h}, 2O-BR_{7-h} and 2O-H_{1-h} structures, and corresponding structures with two O_2 molecules dissociated (i.e., 4O-T_{3-h}, 4O-BR_{7-h} and 4O-H_{1-h}) were displayed in Fig. 2df. The simulated core-level binding energies for 4O-T_{3-h}, 4O-BR_{7-h} and 4O-H_{1-h} structures were displayed in Fig. 4h-j, and each peak was labeled with n : m, which stood for a boron atom coordinated with n boron and m oxygen atoms. It showed that boron atoms coordinated with 3 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 XPS experiment¹².

Interestingly, as shown in Fig. 4b-j, there were some boron atoms coordinated with both oxygen and boron atoms, the core-level binding energies for which located near the middle peak position of XPS experiment¹². 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 the assumption above may be greatly underestimated, and there should be more partially oxidized boron atoms. It agreed to foregoing conclusion that the O_2 molecules chemisorbed and dissociated easily on supported β_{12} borophene, which led to oxidation of many boron atoms.

Based on the analyses above, we proposed a novel B_5O_4 sheet (as shown in Fig. 5ab), derived from the pristine β_{12} borophene unitcell on 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 corelevel binding energies for all boron atoms in the supported B_5O_4 sheet were shown in Fig. 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.

The projected band structure of supported B_5O_4 sheet was calculated. As shown in Fig. 5d, some bands with contributions of boron atoms were crossed by Fermi level, which indicated that B_5O_4 sheet was metallic in nature.



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 supported B_5O_4 sheet (inset is first Brillouin zone) and (e) energy surfaces in the area A. XPS peaks come from experimental results for oxidized supported borophene¹².

The bands contributed by oxygen atoms were much lower than Fermi level, which came from strong covalent B-O bonds. So the metallicity of B_5O_4 sheet 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 Fig. S2a). Interestingly, there appears to be a gapped Dirac cone in the area A (marked in Fig. 5d), the gap for which is bout 0.05 eV. However, the energy surfaces in the area A (displayed in Fig. 5e and Fig. S2b 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 a good way for protection⁵². Free-standing β_{12} borophenes sandwiched by graphenes and BN monolayers were shown in Fig. S3a-b. The mismatch in two structures was close to or smaller than 1%, and the distances between layers were 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 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, due to the enhanced reducibility of the borophene upon the presence of silver substrate. It is found that O_2 molecules prefer to be adsorbed on two hexa-coordinated boron atoms, which tend to dissociate and diffuse along filled-hexagon ribbons, while some oxygen atoms are pined between hexagonal holes. 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. 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 suggest the protection of borophenes from oxygen (e.g., constructing sandwich or layered heterogeneous structures) is therefore essential for their broad applications.

Supporting Information Available

The Supporting Information is available free of charge on the ACS Publications website at DOI:XXXXXX.

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 populations (COHP) curves for B-O and B-O bonds, electron localization function for supported B_5O_4 sheet and optimized β_{12} borophenes sandwiched by graphenes and BN monolayers.

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Graphical TOC Entry

