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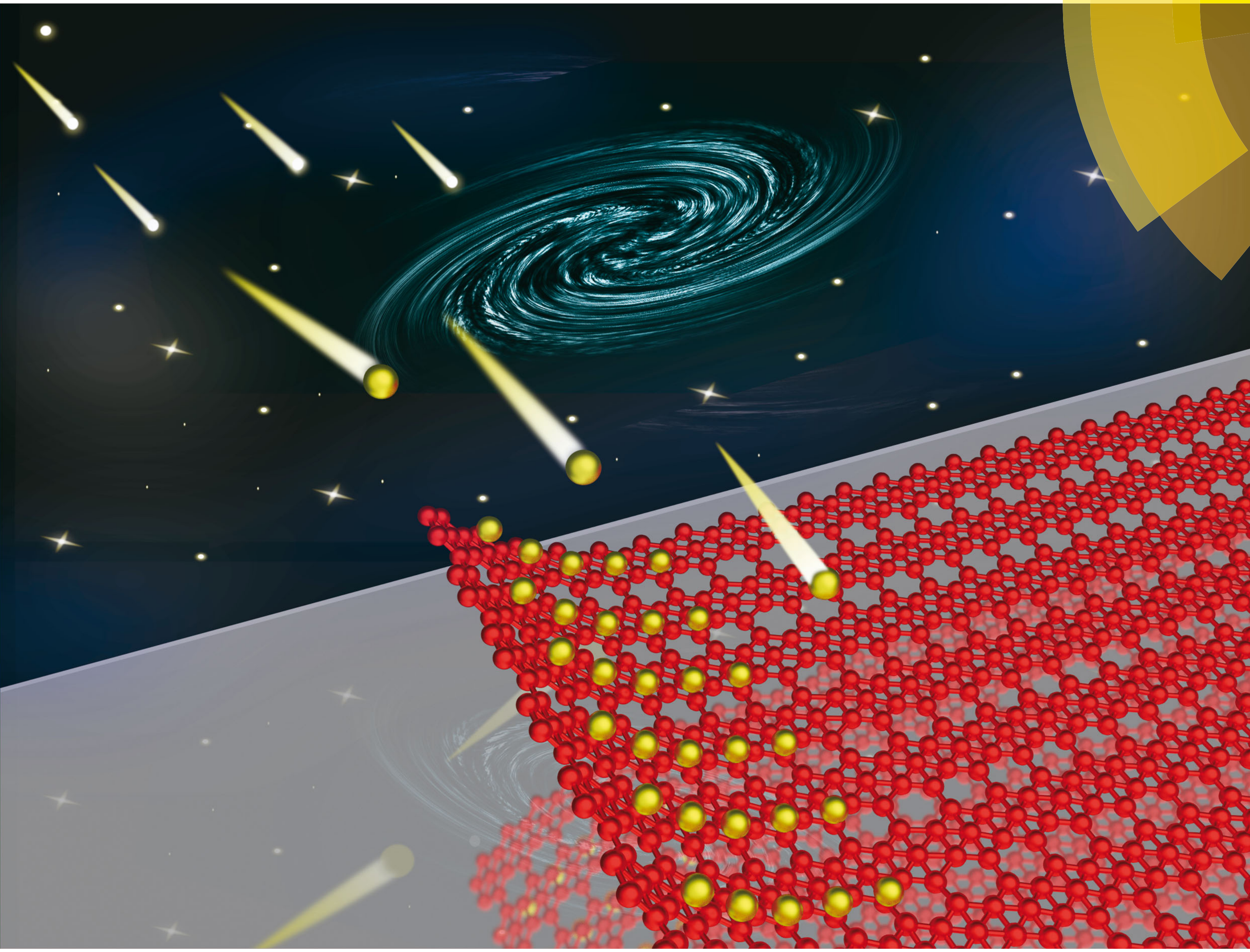

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Exfoliation of borophenes from silver substrates assisted by Li/Mg atoms—a density functional theory study†

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The exfoliation of monolayer borophenes from substrates is deemed a prerequisite for their further applications. Detailed density functional theory calculations performed herein indicate that Li/Mg adatoms evenly distributed on a borophene tend to transform the interaction between borophene and the Ag(111) substrate into van der Waals-like interaction and help to separate them, making the exfoliation of borophenes from substrates much easier. It is also possible for Li/Mg atoms to intercalate below borophene from borophene edges to separate borophene from the substrate. The results obtained in this work may facilitate the exfoliation of borophenes from metal substrates in future experiments.

1. Introduction

Since the first successful experimental preparation of graphene,[1] it has gained extensive attention due to its remarkable electronic, mechanical, optical, and thermal properties.[1–4] It stimulated great interest in other monolayer two-dimensional (2D) materials, some of which have been synthesized in recent years, such as silicene,[5,6] BN monolayers,[7,8] phosphorene,[9] and MoS_2 sheets.[10,11] Most of them have particular properties and significant potential applications.[12–15]

Boron, as the close neighbor of carbon, has rich chemical diversity, the monolayer allotrope of which has drawn a lot of attention in the past few years.[16–18] Though the successful synthesis of single- and multi-walled boron nanotubes (MWBNTs)[19,20] and borospherenes[21,22] combined with several theoretical studies[23,24] suggested the existence of monolayer boron sheets (*i.e.*, borophenes[25]), borophenes were finally experimentally realized on silver substrates very recently.[26,27]

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.[28,29] In addition, it was revealed that borophenes showed remarkable mechanical characteristics, such as very high flexibility, ideal strength and negative Possion's ratio.[30–32] Superconducting behavior was predicted in borophenes.[33] An isolated nickel atom supported on a β_{12} boron monolayer was predicted to be a single-atom bifunctional catalyst for overall water splitting.[34] Due to the significant interaction between borophenes and silver substrates and the chemical reactivity of borophenes, exfoliation and transfer of borophenes to other substrates or devices turn out to be a big challenge.[35] Furthermore, a previous study predicted that topological transformation between hexagonal lattice domains and triangular lattice domains in the boron layer would occur when the concentration of Mg ions in MgB_x (x = 2–16) varied,[36] which indicates that borophenes may turn into another allotrope after exfoliation due to the change in the charge environment. Therefore the exfoliation of borophenes from substrates without phase transition becomes a prerequisite for their further applications.

Theoretical calculations predicted that the adhesion energy between a β_{12} borophene and the Ag(111) substrate is 0.042 eV $Å^{-2}$,[37] which was much larger than the binding energy of graphite (0.012 eV $Å^{-2}$)[38] and monolayer graphene on Cu(111) (0.024 eV $Å^{-2}$),[39] though they were within the same order of magnitude. This implies that β_{12} borophene may be separated from the substrate in a manner analogous to that of graphene if the interaction is weakened. Previous studies have shown that the interaction between graphene and the substrate could be effectively weakened by atom intercalation between them.[40–43] Another study claimed that oxidation made exfoliation of graphene from graphite easier.[44]

Inspired by the these achievements, in this study, we would investigate the exfoliation of a β_{12} borophene from the Ag(111) substrate with and without adsorbed or intercalated atoms using DFT methods. Strong covalent bonding between boron and oxygen atoms may reconstruct even destroyed borophene, while ionic interaction between boron and alkali metal or alkali earth metal atoms would not deform borophene significantly.

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Furthermore, low electronegativities of alkali metal and alkali earth metal atoms would balance the electron deficiency of boron atoms and borophene,[45] which would weaken the interaction between borophene and the substrate and may suppress the charge-driven structural transformation of borophenes.[36] Li and Mg, as most common alkali metal and alkali earth metal elements, respectively, prefer to separate rather than cluster on some substrates,[46,47] which makes them good candidate adsorbed or intercalated atoms for borophene exfoliation. Our study indicated that adsorption of Li/Mg atoms on borophene would weaken the interaction between borophene and the substrate significantly, which made the exfoliation much easier.

2. Methods

All the calculations were carried out within the framework of density functional theory (DFT) as implemented in the Vienna Ab initio Simulation Package (VASP).[48,49] The generalized gradient approximation (GGA) with the Perdew–Burke–Ernzerhof (PBE)[50] exchange correlation functional and projector-augmented wave (PAW) method[51,52] were used. The kinetic energy cut-off for the plane waves was chosen to be 500 eV. The geometries were optimized using the conjugate gradient method until the force acting on each atom fell below a threshold value of 0.01 eV Å^{-1}. A 2 × 2 supercell of β_{12} borophene on the Ag(111) substrate was selected as a basic model for borophene exfoliation, atom adsorption, atom diffusion, atom intercalation and so on. The Ag(111) substrate was modeled by a three-layer slab with only the bottom layer fixed. The concentration (Θ) of adsorbed or intercalated metal atoms was defined as the ratio of the number of metal atoms to that of hexagonal holes. All of the models have a large vacuum spacing (more than 20 Å) to prevent mirror interactions. The Brillouin zones were sampled with 0.1 Å^{-1} spacing in a reciprocal space by the Monkhorst–Pack scheme.[53] The climbing image nudged elastic band (CI-NEB) method[54,55] was used to search transition states.

3. Results and discussion

In this study, β_{12} borophene was selected as the prototype for exfoliation study because β_{12} borophene was the most stable borophene allotrope on the Ag(111) substrate.[56] The binding energy was defined as follows:[44]

$$E_{\text{b}} = \frac{E_{\text{sub}} + E_{\text{borophene}} - E_{\text{tot}}}{A}$$

where E_{tot}, E_{sub} and $E_{\text{borophene}}$ are the energies of the total system, substrate and borophene, respectively, and A denotes the area of the created surface. The binding energy for bare β_{12} borophene supported on the Ag(111) substrate was calculated to be 0.045 eV Å^{-2}, in good agreement with a previous prediction (0.042 eV Å^{-2}),[37] which was much larger than the binding energies of graphite[38] and monolayer graphene on Cu(111).[39] It was maybe due to the charge transfer from the substrate to borophene[27] because of the fact that more electrons are needed for supported borophene compared to freestanding allotropes with lower hole densities.[45]

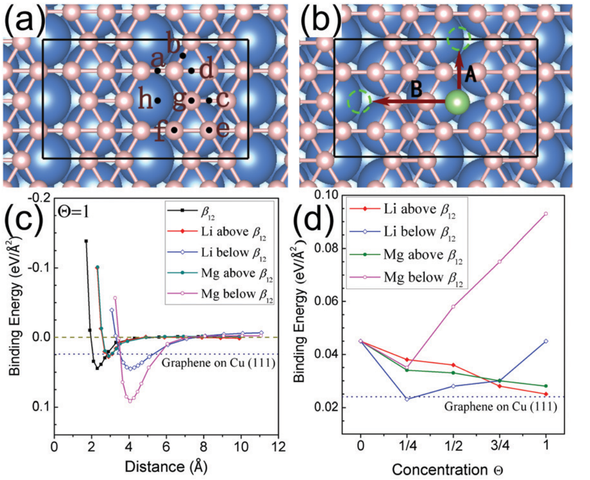

Fig. 1 (a) Adsorption sites on β_{12} borophene supported by the Ag(111) surface. (b) Illustration for two diffusion paths of adsorbate atoms on β_{12} borophene. (c) The binding energies of β_{12} borophene with or without decorated atoms *vs.* the distance between borophene and the substrate surface for Θ = 1. (d) The variation trend of binding energy between decorated borophene and Ag(111) with the change in concentration of Li/Mg atoms. Pink (small), blue (large) and green (medium) balls represent B, Ag and Li/Mg atoms, respectively.

Since adsorbing atoms with low electronegativities (*e.g.*, alkali metal and alkali earth metal atoms) would balance the electron deficiency of boron atoms and supported borophenes, we studied the effect of adsorption of Li/Mg atoms on the exfoliation of borophenes using DFT methods. Eight adsorption sites (as shown in Fig. 1a) were examined to obtain the best adsorption configuration. The adsorption sites could be classified as follows: above the center of the hexagons (h), above the middle of two adjacent boron atoms (a, b, c, and d) and at the top of boron atoms (e, f, and g). The adsorption energy (E_{ad}) is defined as follows:

$$E_{\text{ad}} = \frac{E_{\text{borophene}} + nE_{\text{A}} - E_{\text{borophene}+n\text{A}}}{n}$$

where $E_{\text{borophene}}$, E_{A} and $E_{\text{borophene}+n\text{A}}$ are the energies of the supported borophene, isolated adsorbate atoms and the borophene with adsorbate atoms, respectively, and n = 4 is the number of adsorbed atoms for Θ = 1. Our calculations showed that only adsorbate atoms at e and h sites were stable, while atoms at other sites would slide to the e or h site. The hollow site h was predicted to be the most stable location for Li adsorption (about 2.44 eV).

Previous studies showed that Li atoms preferred to separate rather than cluster on some substrates,[46,47] which indicated that Li atoms may distribute evenly on the borophene. To examine whether it holds true for Li/Mg atoms on β_{12} borophene, the stability of Li_2, Li_4, Mg_2 and Mg_4 clusters on top of one hexagonal hole was studied. Our calculations showed that the Li/Mg atoms indeed tended to distribute evenly on the borophene (see Fig. S1 and S2 in the ESI†). Furthermore, the diffusion of Li atoms between two adjacent hollow sites h was studied. The diffusion energy barriers (E_a) for the two paths A and B (as shown in Fig. 1b) were predicted to be 0.483 eV and 0.726 eV, respectively (Fig. 2a and b). According to transition-state theory, the diffusion could take place easily due to low reaction temperatures (*i.e.*, about 203 K and 305 K estimated by $10^{12}\exp(-E_a/k_BT) \approx 1$),[57] and such a barrier could be overcome by the Coulomb repulsion between Li ions (about 0.718 *e* lost for each Li atom from Bader charge analysis) combined with thermal energy.

The binding energy between β_{12} borophene (with adsorbate Li atoms on each hollow site h, *i.e.*, $\Theta = 1$) and the Ag(111) substrate was calculated to be 0.025 eV Å^{-2}, which was much smaller than that of bare β_{12} borophene on Ag(111) and very close to that of graphene on the Cu(111) substrate[39] (Fig. 1c). The electron loss of the Ag(111) substrate was 0.0011 e Å^{-2} from Bader charge analysis, which was much smaller than that of the Ag(111) substrate with bare borophene (about 0.012 e Å^{-2}). The charge density difference (Fig. S3, ESI†) also showed that the electron loss of the substrate was negligible compared to the charge transfer between borophene and Li atoms. Furthermore, the distance between the borophene base plane and Ag(111) surface increased to 2.90 Å on average from 2.31 Å after adsorption. These results indicated that the adsorption of Li atoms transformed the interaction between borophene and the substrate to van der Waals-like interaction, which would make the exfoliation much easier.

The effect of Mg atom adsorption on the exfoliation of β_{12} borophene was studied in a similar way. Similar to the adsorption of Li atoms, the hollow site h was also the most stable location for Mg atom adsorption (about 1.49 eV). In addition, we also studied the diffusion of Mg atoms on the borophene surface. It was found that the diffusion barriers for paths A and B were 0.554 eV and 0.712 eV, which corresponded to reaction temperatures of 233 K and 299 K, respectively. Therefore, given the effect of Coulomb repulsion and thermal energy, overcoming such low barriers is not difficult. The binding energy between decorated β_{12} borophene ($\Theta = 1$) and the Ag(111) substrate decreased to 0.0279 eV Å^{-2} (Fig. 1c), which also indicated easier exfoliation compared to bare β_{12} borophene. Negligible electron loss was also observed for the Ag(111) substrate (Fig. S3b, ESI†), which was about 0.0066 e Å^{-2} from Bader charge analysis. In summary, our study indicated that the adsorption of Li/Mg atoms on borophene would weaken the interaction between borophene and the substrate significantly, which would make the exfoliation much easier.

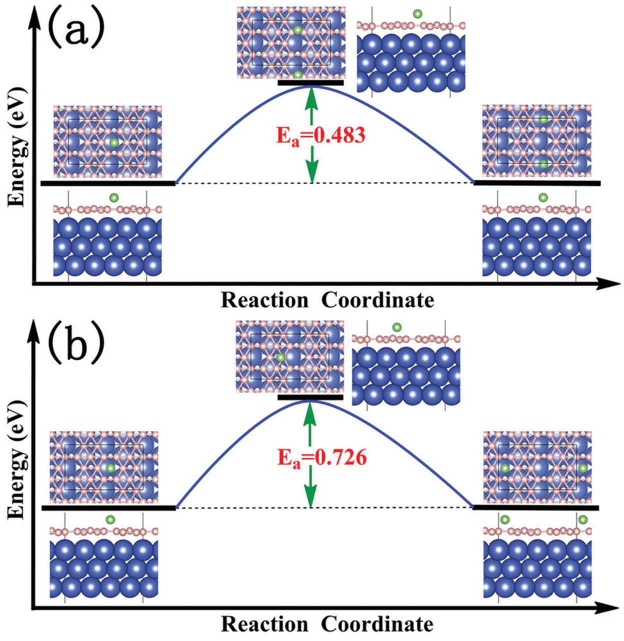

Fig. 2 Diffusion profiles for paths A (a) and B (b).

We also studied the variation trend of the binding energy between decorated borophene and the Ag(111) substrate with a change in the adsorption concentration (Θ) of Li/Mg adatoms (as shown in Fig. 1d). This showed that the binding energy decreased monotonously with the increase of adsorption concentration of Li/Mg adatoms, due to which more Li/Mg adatoms balanced the electron deficiency of borophene better.

It should be noted that the metal atoms may penetrate through the borophene or intercalate below the borophene from edges and lie beneath the borophene, which increases the separation between borophene and the silver substrate and thus may make the exfoliation even easier. The reaction profile for Li atoms penetrating through β_{12} borophene *via* a hexagonal hole is displayed in Fig. 3a. As shown in Fig. 3a, it was an endothermal reaction and a large energy barrier (about 3.023 eV) had to be overcome, which was just a little smaller than that of Li atoms penetrating through graphene (about 3.98 eV).[58] Such a huge barrier corresponded to a temperature of 1264 K according to transition-state theory, which implied a very difficult task. And it was also a hard task for Mg atoms with close or even larger atomic radius.

It may be much easier for atoms to intercalate below borophene from edges than to penetrate through holes due to a much weaker spatial confinement, so the intercalation of Li/Mg atoms from edges was studied. We investigated the diffusion of Li and Mg atoms under borophene, the paths (C and D) for which are shown in Fig. 3b. Our results showed that the diffusion barriers for Li atoms along C and D directions were 0.288 eV and 0.310 eV, respectively, and the corresponding values for Mg atoms were 0.362 eV and 0.731 eV. These results suggested that the diffusion path along adjacent holes would be much easier than that perpendicular to it, and the same tendency was observed for adsorbed atoms. It could be interpreted from two aspects: first, diffusion along adjacent holes would lift less boron atoms compared to the other direction; and second, diffusion along adjacent holes would encounter less boron atoms with opposite charges.

As a result, intercalation of Li and Mg atoms below β_{12} borophene from armchair edges would be easier than those from zigzag edges. The reaction profile for Li/Mg atom intercalation below β_{12} borophene from armchair edges is shown in Fig. 4a and b. The intercalating energy barrier for Li atoms was predicted to be 1.227 eV, indicating a reaction temperature of 515 K, which was lower than the typical preparation temperature of β_{12} borophene on the Ag(111) substrate (about 600 K[27]).

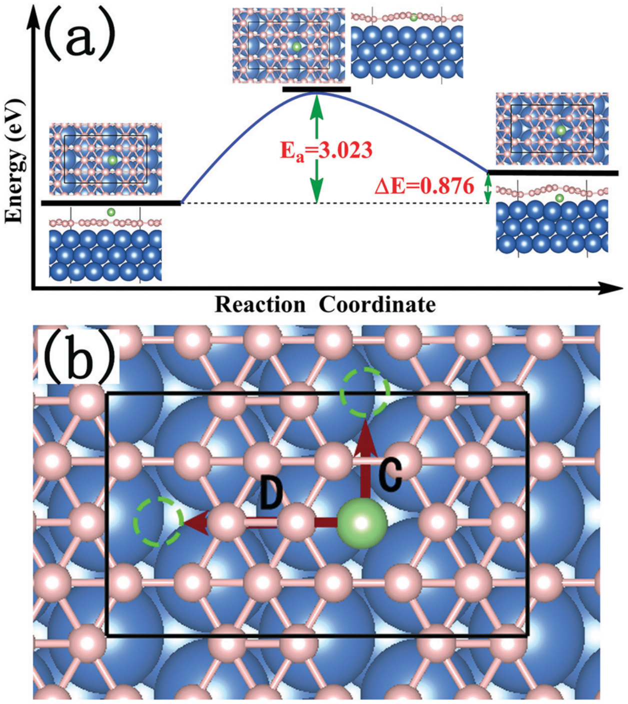

Fig. 3 (a) Reaction profile for Li atom penetrating through β_{12} borophene. (b) Illustration for two diffusion paths of metal atoms beneath β_{12} borophene.

Meanwhile, the energy barrier for Mg atom intercalation below borophene from armchair edges was predicted to be 1.053 eV, indicating a reaction temperature of 442 K, which was also lower than the typical preparation temperature of β_{12} borophene. The binding energy between β_{12} borophene (with intercalated Li atoms under each hexagonal hole, *i.e.*, Θ = 1) and the Ag(111) substrate was calculated to be 0.0448 eV Å^{-2} (Fig. 3c), which was a little smaller than that of bare β_{12} borophene on Ag(111). Due to the electronegativity difference, the borophene and the Ag(111) substrate gained 0.036 e Å^{-2} and 0.020 e Å^{-2} electrons, respectively, while Li atoms lost 0.056 e Å^{-2} electrons. So the Coulomb attraction between the Ag(111) substrate and Li atoms replaced the attraction between the Ag(111) substrate and borophene. The separation between the Ag(111) substrate and borophene increased to 4.078 Å, and it reduced to 4.058 Å in the case of Mg atom intercalation. These results indicate that the intercalation of Li/Mg atoms did not reduce the binding energy significantly due to the emerging Coulomb attractions between Li/Mg atoms and the silver substrate, but the substrate and borophene could be separated below the typical preparation temperature of borophene.

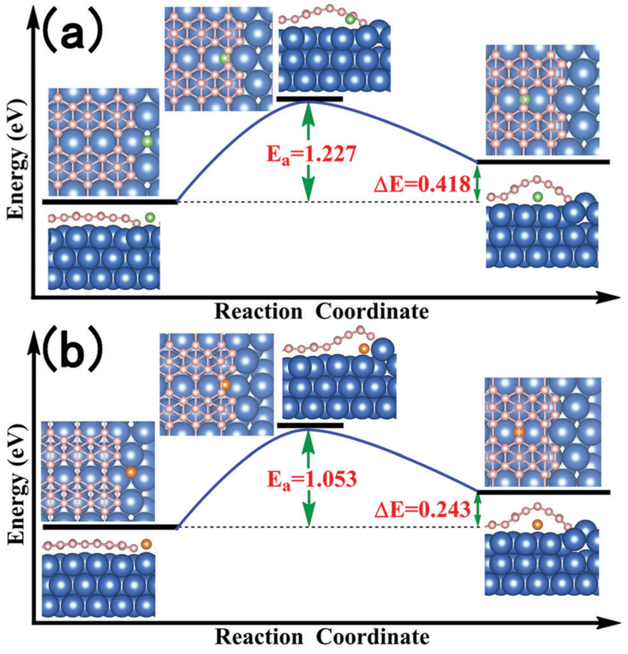

Fig. 4 Reaction profiles for (a) Li and (b) Mg atoms intercalating below β_{12} borophene from armchair edges.

The variation trend of the binding energy between decorated borophene and the Ag(111) substrate with a change in the intercalation concentration (Θ) of Li/Mg atoms (as shown in Fig. 1d) was studied. In contrast to the monotonous trend in the case of adsorption, the binding energy between borophene with intercalated Li/Mg atoms and the substrate reached the minimum value at Θ = 1/4 and the binding energy in the case of Li atom intercalation (Θ = 1/4) even fell below that of graphene on Cu(111). This indicated that low-concentration intercalated Li/Mg atoms performed better to separate the borophene and the substrate, owning to the fact that the intercalated atoms lifted the borophene without strong Coulomb attraction appearing compared to the case of Θ = 1.

The removal of metal atoms from borophene may be important for its applications. Our calculations showed that the adsorption energy of single Li/Mg atoms on freestanding β_{12} borophene was 3.11/1.96 eV, which would be reduced to 2.66/1.08 eV in the case of supported β_{12} borophene on the Ag(111) substrate. This indicated that the interaction between metal adatoms and the borophene could be weakened by the substrate due to which the substrate would balance the electron deficiency of borophene. Furthermore, gate voltage control may be another method to weaken the interaction for which the electron deficiency of borophene could be tuned by charge doping.[59] Given the significant charge of Li/Mg adatoms and low diffusion barriers, in-plane electric field may be a good method to drive Li/Mg adatoms away from the borophene.

4. Conclusions

We systematically investigated the exfoliation of β_{12} borophene from the Ag(111) substrate with and without adsorbed or intercalated Li/Mg atoms using DFT methods. Our results indicated that Li and Mg adatoms tended to separate and distribute evenly on the borophene due to which the low diffusion barriers (about 0.483–0.726 eV) could be overcome by the Coulomb repulsion between adatoms combined with thermal energy. These Li/Mg adatoms transformed the interaction between borophene and the substrate into van der Waals-like interaction, which would make the exfoliation much easier. Though it was very difficult for Li/Mg atoms to penetrate through the holes of borophene, it is possible for them to intercalate below borophene from armchair edges below the typical preparation temperature of β_{12} borophene. The intercalated Li/Mg atoms separated borophene and the substrate, and low-concentration intercalation performed better than the high-concentration intercalation for separation, though it led to Coulomb attraction between borophene and Li/Mg atoms as well as that between Li/Mg atoms and the silver substrate. The results on β_{12} borophene may also hold true for other borophenes due to their geometrical and bonding similarity. Our study proposed a preliminary exploration on the exfoliation of borophenes, which would facilitate the exfoliation of borophenes from metal substrates in future experiments, and may promote their application study in Li-ion batteries.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

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