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Introduction

In the past few decades, with the rapid development of experimental technologies, many novel materials were realized.^{1,2} For example, two-dimensional materials have aroused widespread interest since the preparation of graphene.³ Graphene has many outstanding properties, such as unique chemical properties, high mechanical durability, and excellent carrier mobility,^{4–7} which make it play an important role in many fields, such as new energy batteries, electronic mobile devices and aerospace devices.^{8–10} In the meantime, scientists continue to search for other two-dimensional materials.^{11–13} Among them, boron monolayer materials have attracted extensive attention.^{14,15}

Boron, a close neighbour of carbon, is an important element with both metallic and nonmetallic chemical characteristics. Due to the electron-deficient nature of boron, multicenter bonds are typical of boron-based materials.¹⁶ In 2015, Mannix *et al.* prepared buckled triangular borophene (δ_6).¹⁷ Meanwhile, β_{12} and χ_3 borophenes were experimentally realized by Feng *et al.*¹⁴ It should be noted that two-dimensional borophenes tend to be easily oxidized,^{18,19} which makes further study of their related

Compression-induced crimping of boron nanotubes from borophenes: a DFT study[†]

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Several borophenes have been prepared successfully, but the synthesis of boron nanotubes is still very difficult. Our results suggest that the high flexibility of borophene in combination with van der Waals interactions makes it possible to coil boron nanotubes from rippled borophenes, which is confirmed by *ab initio* molecular dynamics simulations. The plane structures transform into rippled structures almost without any barrier under very small compression and weak perturbations like molecular adsorption. The compression energies of the rippled structures increase linearly and slowly with the increase of the compression. This suggests how the geometry of the borophene evolves with compression. Based on the evaluation of the free energy of hydrogen adsorption, a stronger compression suggests the improved hydrogen evolution performance of the borophene and even makes it better than Pt catalysts. Meanwhile, good hydrogen evolution performance is also suggested for boron nanotubes. Our results suggest a novel preparation method for boron nanotubes from borophenes and a possible way to improve their hydrogen evolution performance.

properties in experiments difficult. As a result, first-principles methods were employed to investigate the mechanical properties,²⁰ superconductivity,²¹ stability,²² electronic properties²³ and magnetism²⁴ of borophenes. Besides, borophenes were also predicted to serve as good non-metallic electrocatalysts for the hydrogen evolution reaction (HER).²⁵

Besides borophenes, boron nanotubes (BNTs) have also gradually attracted extensive interest. Both single- and multi-walled boron nanotubes have been prepared in experiments.^{26,27} It was found that multi-walled boron nanotubes could serve as stable high-efficiency luminescent devices.²⁸ In theoretical aspects, boron nanotubes were predicted to be highly conductive,^{29,30} indicating potential applications in the fabrication of novel nanoelectronic devices.^{24,30,31} In short, boron nanotubes have some excellent potential applications, but they are very difficult to prepare in experiments, and few follow-up experimental studies were reported. Given many studies on crimping two-dimensional monolayers into nanotubes,^{32–35} borophenes may serve as good precursors for preparing boron nanotubes.

Hydrogen, as a pollution-free renewable energy storage medium, has drawn considerable attention in the past few decades. Due to the high overpotential in the production of hydrogen by the electrolysis of water, cheap and effective catalysis for the hydrogen evolution reaction (HER) was in urgent need. It was reported that the calculated adsorption free energies of an H atom on the three sites of free-standing β_{12} borophene are 0.10–0.23 eV, indicating good intrinsic catalytic activity for the HER.²⁵ As is well known, electronic properties would be modulated by applied strain or compression,



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[†] Electronic supplementary information (ESI) available: β_{12} borophene with an H adatom and H₂; ELF of β_{12} borophene; geometries of β_{12} borophene under compression; band structures of β_{12} borophene under compression; adsorption sites of an H adatom; AIMD simulations of borophene and boron nanotubes with OH. See DOI: https://doi.org/10.1039/d2cp01824a

so the HER performance of compressed β_{12} borophene was examined.

In this paper, we systematically studied the effects of compression on the structure and properties of β_{12} borophene. Different compression directions and four compression modes were considered. Given the important role of strain engineering in the modulation of the electronic properties and catalytic performance of materials,^{36–40} work functions and HER activity for the borophene under different compressions were also investigated. It was found that coiling the borophene into boron nanotubes under high compression was practicable, and the HER activity of borophenes would be improved under appropriate compression.

Computational methods

All the calculations were performed using Vienna Ab initio Simulation Package (VASP 5.4).^{41,42} The projector augmented wave (PAW)^{43,44} pseudopotential method and Perdew–Burke–Ernzerhof (PBE)⁴⁵ exchange correlation functional were employed. The cutoff energy of the plane waves was set to 450 eV. Grimme's DFT-D3^{46,47} van der Waals (vdW) correction with Becke–Johnson (BJ) damping was employed. The convergence criteria for the energy and force were 10^{-4} eV per cell and 0.01 eV Å⁻¹, respectively. The vacuum spacings for the pristine borophene and highest compression cases are larger than 21 and 12 Å, respectively, and the minimum distance between boron atoms in neighbouring mirror interactions. The Brillouin zones were sampled with a $2\pi \times 0.02$ Å⁻¹ spacing in the reciprocal space by the Monkhorst–Pack scheme.⁴⁸

The compression is defined as follows:

$$c = \frac{L_0 - L}{L_0} \tag{1}$$

where *L* and *L*₀ represent the lattice constants of compressed and pristine borophenes, respectively. The compressions in *a* and *b* directions are represented by ε_a and ε_b , respectively. When a particular lattice vector is compressed under loading conditions, the lattice vector in the other direction relaxes completely for the sake of the Poisson effect. The compression energy (*E*_c) for the borophene is defined as follows:

$$E_{\rm c} = \frac{E_{\varepsilon}}{N} - \frac{E_{\varepsilon=0}}{N},\tag{2}$$

where E_{ε} represents the energy of each structure under ε , N represents the total number of boron atoms, and $E_{\varepsilon=0}$ represents the energy of the pristine borophene without compression.

Ab initio molecular dynamics $(AIMD)^{49}$ simulations in canonical ensemble (*NVT*) were performed at 300 K to investigate the crimping progress of the borophene. The total simulation time was 5 ps with a timestep of 0.5 fs and the temperature was controlled using a Nose–Hoover thermostat. In the above simulations, the lattice was doubled in the uncompressed direction, and a large vacuum spacing was added in the compressed direction at the boundary. As a result, our models

for these simulations were one-dimensional borophene nanoribbons. The root mean square deviations (RMSDs) were calculated using the VMD package.⁵⁰

The free energy of hydrogen adsorption ($\Delta G_{\rm H}$) is usually used to evaluate hydrogen evolution reaction (HER) catalytic activity. It was calculated based on the computational hydrogen electrode (CHE) model proposed by Nørskov *et al.*, where the chemical potential of an electron and proton pair is half of the free energy of H₂.^{51,52} According to this method, $\Delta G_{\rm H}$ can be defined as⁵³

$$\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta H_{\rm vib} + \Delta Z P E - T \Delta S + \Delta G_{\rm U} + \Delta G_{\rm pH}, \qquad (3)$$

where $\Delta E_{\rm H}$ is the differential hydrogen chemisorption energy from the DFT calculations, *T* is room temperature (298.15 K), and $\Delta H_{\rm vib}$, ΔZPE and ΔS represent the changes in vibrational enthalpy, zero point energy and entropy, respectively. $\Delta G_U = -eU$ can be used to show the influence of applied electrode potential *U*, where *e* is the elementary charge transferred. $\Delta G_{\rm pH}$ stands for the free energy correction of pH. The effect of *U* and pH was not taken into account in our study (U = 0, pH = 0). The vibrational enthalpy of an H adatom and half of the vibrational enthalpy of H₂ are also very small and comparable ($\sim 0.02 \text{ eV}$), so they were neglected. As a result, the free energy of hydrogen adsorption ($\Delta G_{\rm H}$) can be calculated as follows:^{52,54}

$$\Delta G_{\rm H} = \Delta E_{\rm H} + \Delta Z {\rm PE} - T \Delta S. \tag{4}$$

The contribution of the vibrational entropy of an H adatom is negligible (~0.01 eV), so we take the entropy change of hydrogen adsorption as $\Delta S_{\rm H} \cong -1/2S_{\rm H_2}^{\theta}$, where $S_{\rm H_2}^{\theta}$ is the entropy of a gaseous hydrogen molecule under standard conditions. The zero point energy and vibrational entropy were calculated from the frequencies using the VASPKIT code.⁵⁵

Results and discussion

How the geometry of the borophene evolved with the compression was unknown, so four possible structural modes were considered. They are a plane structure and ripple structures with periods of 6, 4 and 2 units in the compressed directions (referred to as ripple-6, ripple-4 and ripple-2, respectively). Of course, there are infinitely many ripple structures with larger units, but we only considered ripple structures with up to 6 units, which was enough to reflect the trend. The lattice in the uncompressed direction was also expanded; as a result, a 6 \times 2 supercell was taken for plane-a and ripple-6a modes, while ripple-4a and ripple-2a modes shared the same model of a 4 \times 2 supercell (Fig. 1a–d). The corresponding model structures for the *b* direction are shown in Fig. S1 of the ESI.† Ripple structures were observed in graphene, which tended to increase its adsorption ability.⁵⁶ Similar trends were also observed for the adsorption of H₂ on carbon nanotubes.⁵⁷

The compression energies for different modes in different directions are displayed in Fig. 2. When the borophene was compressed in the plane-*a* mode, the compression energy increased drastically until it was reconstructed into another



Fig. 1 Top and side views of compressed β_{12} borophene under $\varepsilon_a = 20\%$ for (a) plane-*a*, (b) ripple-6*a*, (c) ripple-4*a* and (d) ripple-2*a* modes.

phase with a χ_3 borophene fragment under $\varepsilon_a > 20\%$, which was composed of hexagonal holes and double chains (marked with the red circle in Fig. 2a). It behaved in a similar way regardless of the direction of compression (a or b), which indicated the significant rigidity of the in-plane multicenter bonds (e.g., 2c-2e, 3c-2e or 4c-2e σ bonds in Fig. S2, ESI⁺) under higher compressions. The second derivatives $\partial E_c^2/\partial^2 \varepsilon$ for plane-a and plane-b modes were 27.54 and 21.34 eV, respectively, which indicated that the in-plane stiffness in direction a was larger than that in direction b. It showed an opposite trend to the pristine β_{12} borophene, the corresponding Young's moduli for which were 189 and 210 N m⁻¹, respectively.⁵⁸ Meanwhile, the compression energy increased linearly with compression slightly for ripple-6a, ripple-4a and ripple-2a modes, the slopes for which were 0.05, 0.12 and 0.28 eV, respectively. The corresponding slopes were 0.15, 0.21 and 0.39 eV for ripple-6b, ripple-4b and ripple-2b modes, respectively. This suggested stronger bending stiffness in the b direction, which was also opposite to the predicted bending stiffness for pristine β_{12} borophene (Dx = 0.56 and Dy = 0.39).⁵⁸ The reason for the reversal may be due to the significant Poisson effect under high compressions. Generally speaking, the ripple structures were more stable than the plane structures, and the ripple-6a and ripple-6b modes were most preferred and retained their geometries under $\varepsilon_a < 70\%$ and $\varepsilon_b < 70\%$, respectively (Fig. S3 and S4, ESI[†]).



Fig. 2 Compression energies (E_c) as a function of the compression strains (*z*) along (a) *a* and (b) *b* directions.

Fig. 2 also shows that the ripple-2*a* and ripple-4*a* modes were less stable than the ripple-6*a* mode, which has a longer wave period. The same behavior was observed for the compressions in the *b* direction. These results indicated that the curvature energy would dominate the compression energy before its reconstruction. Interestingly, the borophene under $\varepsilon_b = 50\%$ in the ripple-2*b* mode would transform into a bilayer structure (Fig. S4 (ESI[†]) and inset in Fig. 2b) and became much more stable.

Besides thermodynamic stability, we relaxed the plane borophene with an H adatom and H₂ without or with a small compression ($\varepsilon_a = 2\%$), to explore the effect of small perturbations. As shown in Fig. S5 (ESI†), H/H₂ adsorption distorted the pristine borophene a little. However, once a small compression was applied, the plane structure transformed into a ripple structure almost without barrier. This meant that small perturbations like weak molecular adsorption could drive such a transformation for compressed borophene. The discussions above suggested how the compressed borophene evolved with the compression.

Since ripple-6a and ripple-6b were the most stable forms under compressions, we investigated the effect of the compressions on their band structures and work functions (before reconstruction). At the same time, the plane borophene (before reconstruction) was also calculated for comparison. As shown in Fig. S6 (ESI^{\dagger}), the borophene in ripple-6*a*/*b* and plane modes remained metallic in character under compression. Meanwhile, the calculated work function of pristine β_{12} borophene was 4.96 eV (as shown in Fig. 3a and b), in agreement with a previous study (4.90 eV).⁵⁹ It was higher than those of graphene $(4.50 \text{ eV})^{60}$ and graphenylene (4.84 eV),⁶¹ but lower than that of phosphorene (5.04–5.16 eV).⁶² The work functions of the plane structures decreased with compression as expected, due to the suppression of the in-plane bonds and weaker binding of electrons on the surface. But they were generally higher than the work functions of β_{12} -BNT(6,0) and β_{12} -BNT(0,6) (about 4.16 and 4.60 eV, respectively) before reconstruction ($\varepsilon < 25\%$). Surprisingly, the work function of the ripple-6a borophene linearly increased with compression and was much higher than that of β_{12} -BNT(6,0). A similar curvature-induced anomalous enhancement in the work function⁶³ was also observed in compressed α -PC³⁴ and MoS₂ nanosheets.⁶⁴



Fig. 3 Relationship between the work functions of β_{12} borophene and the compressions (*c*) along (a) *a* and (b) *b* directions.

Paper

A previous experimental study suggested that nanotubes could be formed by strain-induced rolling of In_xGa_{1-x}As-GaAs membranes.33 Moreover, the formation of phosphorus carbide (PC) nanotubes from the rippled PC monolayer was also predicted.³⁴ Given the high flexibility of the borophene, NVT ab initio molecular dynamics (AIMD) simulation at 300 K was performed to examine whether it was a feasible way for the formation of boron nanotubes. The energy and RMSD evolutions of the compressed ripple-6a borophene nanoribbon $(\varepsilon_a = 65\%)$ during the AIMD simulation are displayed in Fig. 4. It showed that the energy gradually decreased with time, and the edges of the nanoribbon got close to each other easily. The edges got connected in 1.0 ps, then the atoms vibrated in the breathing mode of a nanotube. The detailed evolution of the geometry is shown in Movie S1, ESI.[†] Similar behaviour was observed for the ripple-6b borophene nanoribbon under $\varepsilon_{\rm b}$ = 60% and 65% (as demonstrated in Movie S2, ESI⁺). It should be noted that the open bonds helped in connecting the edges of the nanoribbon when they were close enough, due to the short range of chemical bonding. However, the high flexibility and van der Waals interactions played a dominant role, given the large separation between the edges (Fig. 4) before connection. Otherwise, the ribbon would bounce off quickly and became a flat ribbon to reduce the curvature energy. Our results revealed the possibility of formation of boron nanotubes from compressed borophenes.

The curvature of the sheets tends to enhance the adsorption of molecules,⁵⁷ so the HER performance of boron nanotubes and compressed β_{12} borophene was investigated. There are 3 typical sites for hydrogen adsorption (Fig. 5a), and we examined their adsorption free energies on different parts of the compressed ripple-6*a* borophene ($\varepsilon_a = 20\%$). As shown in Fig. S7 and Table S1 (ESI†), the top part generally behaved better than the slope and bottom parts for the HER activity, maybe due to its highest curvature, so subsequent calculations were based on the adsorption sites on the top part. The calculated free energies of hydrogen adsorption (ΔG_H) at the three sites



Fig. 4 The energy and RMSD evolutions of the compressed ripple-6*a* borophene nanoribbon ($\varepsilon_a = 65\%$) during the AIMD simulation at 300 K. Some inset snapshots are displayed to illustrate the transformations. The separation between edges before connection is labelled.



Fig. 5 (a) Adsorption sites on β_{12} borophene, (b) volcano curve of exchange current (i_0) as a function of the free energy of hydrogen adsorption ($\Delta G_{\rm H}$), and the relationship between $\Delta G_{\rm H}$ and compressive strain (ε) along (c) *a* and (d) *b* directions.

of pristine β_{12} borophene were 0.11, 1.12 and 0.26 eV (Fig. 5b), agreeing well with those in a previous study (0.10, 1.13 and 0.23 eV, respectively).²⁵ In order to explore the intrinsic state of electrons during the HER process,⁵² the exchange current i_0 was calculated to describe the HER kinetics under the equilibrium potential U = 0 and pH = 0 conditions as follows:

$$\dot{t}_0 = -ek_0 \frac{1}{1 + \exp(|\Delta G_{\rm H}|/k_{\rm B}T)},$$
 (5)

where k_0 is the reaction rate constant at zero overpotential, $k_{\rm B}$ is the Boltzmann constant, and *T* is the temperature (298.15 K). For illustrative purposes, k_0 was set to 1.⁶⁵ Hence, a volcano curve was obtained to compare the HER activities on the borophene (Fig. 5b). The HER activity can be quantitatively evaluated from the position of $\Delta G_{\rm H}$ and $\log(i_0)$ with respect to the volcano peak. The closer the position to the volcano peak, the better the HER activity of the catalyst. It was found that the adsorption free energy of H adatoms would decrease when the borophene was compressed, which tends to improve the HER performance of β_{12} borophene (Fig. 5b–d).

The bonding between the H adatom and adjacent B atoms was investigated by integrated crystal orbital Hamilton population (ICOHP)⁶⁶ and density derived electrostatic and chemical bond order (DDEC BO).⁶⁷ Taking the S₁ site for example (Fig. 6), the total –ICOHP and DDEC BO for B–H bonds at the S₁ site mainly increased with the increase of compression in both *a* and *b* directions, indicating the enhancement of the bonding strength, which was in agreement with the trend of the adsorption free energy. The H adatom remained directly above the top atomic chain under ε_b (Fig. 6d), so only s–p_z hybridization was observed for the B–H bond. In contrast, the B–H bond was inclined under ε_a (Fig. 6c); as a result, the s–p_x hybridization increased with ε_a . The slight enhancement of B–H bonds under compression would improve the HER performance and avoid too tight binding of H adatoms. In detail, when the borophene



Fig. 6 Relationship between –ICOHP/DDEC BO for B–H bonds at the S₁ site and compressive strain (ε) along (a) *a* and (b) *b* directions. The compressed (c) ripple-6*a* and (d) ripple-6*b* borophenes ($\varepsilon_{a/b}$ = 30%) with an H adatom on the S₁ site.

was compressed in the *a* direction ($\varepsilon_a \leq 30\%$), the hexacoordinated boron (S₂) showed very poor HER performance, while it was further improved for S₁ and S₃ sites (very close to zero). The $\Delta G_{\rm H}$ values of S₁ and S₃ sites (about -0.05 and 0.04 eV, respectively) on compressed ripple-6*a* borophene ($\varepsilon_a = 30\%$) were closer to 0 eV than the Pt(110) (-0.12 eV) and Mo(1010) edges of MoS₂ with 50% coverage (0.12 eV) (Fig. 5b), which have been proved to have good HER catalytic activity.68-70 Meanwhile, the HER performance of the S₁ and S₂ sites of ripple-6b borophene under $\varepsilon_b \leq 30\%$ was also improved, while the H adatom at the S₃ site was bound too tight. Interestingly, the HER performance of β_{12} -BNT (6,0) and β_{12} -BNT (0,6) was also very good. Generally speaking, the S1 site maintained good HER performance under different compressions, and the compressions in a large range would improve the HER performance of some sites.

The stability of the catalyst is also very important. It was reported that the β_{12} borophene remained stable in solution with Cl⁻ anions.⁷¹ We also simply examined the adsorption of OH on the plane β_{12} borophene and nanotube using AIMD simulations at 300 K (Fig. S8, ESI†). It showed that the borophene and nanotube were not destroyed and OH remained adsorbed to the original boron atom in 10 ps.

Conclusions

We investigated systematically the evolution of the geometries and electronic properties of β_{12} borophene under high compressions using first-principles methods. Our results suggested that the plane structures transformed into rippled structures almost without barrier under very small compression and weak perturbations like molecular adsorption. The compression energies of the rippled structures increased linearly and slowly with the increase of the compression. This suggested how the

geometry of the borophene evolved with the compression. Similar behaviors were observed in both directions, but the relative in-plane and bending stiffnesses in the two directions were different to those free of compression, as a result of a significant Poisson effect under high compressions. A curvatureinduced anomalous enhancement in the work function was observed. The high flexibility of the borophene in combination with van der Waals interactions made it possible to coil boron nanotubes from rippled borophenes, which was confirmed by ab initio molecular dynamics simulations. Bonding analysis showed that compressions would decrease the adsorption free energy of H adatoms slightly. As a result, a stronger compression suggested the improved hydrogen evolution performance of the borophene and made it better than Pt catalysts. Meanwhile, good hydrogen evolution performance was also suggested for boron nanotubes. Our results suggested a novel preparation method for boron nanotubes from compressed borophenes and a possible way to improve their hydrogen evolution performance.

Conflicts of interest

There are no conflicts to declare.

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