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Two-Dimensional Boron Sheets as Metal-Free Catalysts for Hydrogen Evolution Reaction

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ABSTRACT

Current metal-free catalysts for hydrogen evolution reaction (HER) are mainly carbon-based. In this work, HER catalytic activity on two dimensional (2D) boron sheets (α and β_{12}) are explored using periodic density functional theory. Using the binding free energy of H (ΔG_{H^*}) as the descriptor, we found that both α and β_{12} sheets present superior activity, with ΔG_{H^*} being close to zero. It is expected that 2D boron sheets would be a promising metal-free catalyst in electrolysis of water and may offer novel thoughts for the design of new catalysts for other reactions.

Favorable catalysts play an important role in the electrochemical water splitting reaction for hydrogen production.^{1,2} So far, noble metal materials have been regarded as the most efficient electrocatalysts owing to their excellent thermodynamics and kinetics in the electrocatalytic hydrogen evolution reaction (HER).³⁻⁵ However, the limited resources and high cost of noble metals have hampered the viability of large-scaled commercialization.⁶ In addition, noble metals also face other problems, such as migration, loss of active surface area and detrimental environmental effects.⁷ Therefore, Pt-comparable catalysts, particularly two-dimensional (2D) structures, have been extensively explored, including carbides,⁸⁻¹⁰ transition metal dichalcogenides,¹¹⁻¹³ metal organic frameworks (MOFs),¹⁴ carbon nanotube,¹⁵ and doped and defective graphene.^{16,17} Although those 2D structures offer large surface areas, the catalytic sites often origin from the edges, defects, or embedded dopants or metal, rather than the inherent basal planes; as a result, the loading of active sites over specific weight is often low.^{9,12} External strain energy can be helpful to improve it without introducing new components,¹⁸ but the catalysis performance is sensitive to the degree of deformation and can be hardly durable if the strain energy cannot be accurately controlled and maintained.

Recently, 2D boron monolayer has been theoretically predicted and experimentally synthesized on single crystal Ag(111)¹⁹ and Cu(111)²⁰ substrates under ultrahigh-vacuum conditions, gaining widespread attention because of their potentially low cost, large surface area and unique catalytic activities,²¹ together with excellent mechanical,²² thermal,²³ electrical properties.²³⁻²⁵ Similar to carbon, the neighboring boron element also exhibits honeycomb-like 2D structures, but differently, the unit cell of boron sheet composed of triangular and hexagonal motif has been identified to be energetically more stable than those of only triangular lattices or hexagonal lattices,²⁶⁻²⁸ which can be viewed as hole-doped triangular lattices and may bring rich chemistry. Among many predicted

structures, the α -sheet was confirmed to be the most stable structure,²⁹ and β_{12} sheet can be produced readily on Ag surface by direct evaporation of pure boron source.¹⁹ Both sheets have typically porous characteristic structure that can provide sufficient surface space and active atoms. Until now, these boron sheets have demonstrated promising applications in superconductor,³⁰ hydrogen storage,³¹ and oxygen evolution reaction.²¹ In our work, we perform first-principles calculations to investigate boron sheets catalysts for HER activity. As demonstrated below, boron sheets can offer excellent HER catalysis performance, being comparable or even better than those reported for noble metal and metal-free catalysts.

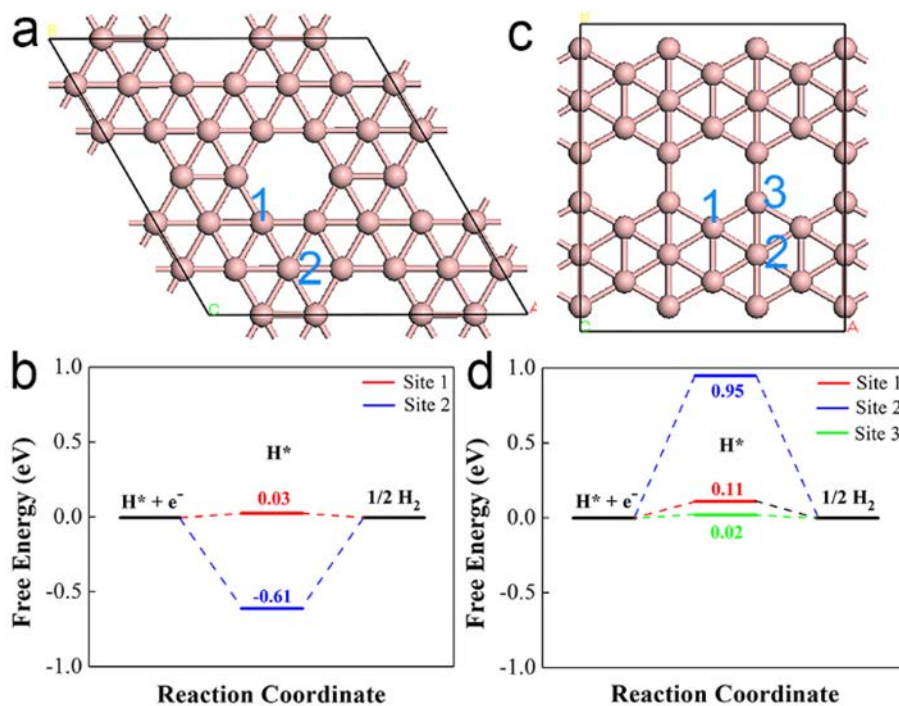


Figure 1. Models and calculated HER performance: (a) α -sheet supercell, (c) β_{12} sheet supercell, and the calculated free energy diagram for the formation of single H_2 at equilibrium on the different sites: (b) α -sheet, (d) β_{12} sheet.

Our calculations start from the early studies of boron sheets,^{28,32} $2 \times 2 \times 1$ supercell for α and $3 \times 2 \times 1$ supercell for β_{12} have been employed, consisting of 32 and 30 boron atoms, respectively. All structures are fully optimized under the scheme of density functional theory, as described in the Supporting Information. Optimized structures are shown in the Fig. 1a, c, which clearly keep perfect monolayer structural characteristics. The triangular and hexagonal motifs and the resulting porous structural characteristic of this “hexagonal hole” could provide lowly coordinated sites for HER. Due to the difference in coordination numbers, boron atoms have been classified as different types, as labelled as Fig. 1. Following early studies,¹³ the Gibbs free energies of H-adsorption, ΔG_{H^*} (see Table S1), has been employed to evaluate the catalysis performance of different sites. Using standard hydrogen electrode (SHE) as the energy reference, HER catalysts with $\Delta G_{H^*} \sim 0$ eV has been targeted in terms of energy efficiency.⁹ More positive ΔG_{H^*} suggests that the catalyst exhibits relatively weak stabilization for the protons bonded, while the hydrogen release will be slow under bigger negative ΔG_{H^*} . Calculated ΔG_{H^*} for different sites has been presented in Fig. 1b,d, according to which both site-2 of α and β_{12} shows poor HER performance, while site-1 in α and site-1&3 in β_{12} offer nearly-zero ΔG_{H^*} , indicating a superior HER activity. Apparently, such high performance origins from the unsaturated nature of boron, as site 1 (in both cases) and site 3 are five- and four-coordinated, while poorly performed site-2 is fully coordinated. Therefore, lowly coordinated boron has been identified as active sites for HER, similar as edge sites of MoS_2 monolayers.¹¹

Although a large variety of planar 2D boron structures with competitive cohesive energy, the experimental realization 2D boron sheets remains a challenge. This problem maybe hamper the further large-scale application of these technologies. Currently, boron sheets are synthesized on specific metal surfaces, like Ag and Cu.^{19,20} In our case, as-grown β_{12} sheet on metal substrates has

been modelled with β_{12} on Ag(111) and Cu(111). The optimized geometries are shown in Fig. 2a, b, respectively, according to which boron-metal substrate distance is around 2.49 and 2.13 Å. The B-metal distance is comparable to that in the known B-metal alloys and suggests moderate covalent bonding interaction between boron and metal atoms.³³ HER over three sites have been further investigated as shown in Fig. 2c, d. With respect to free standing boron sheets (see Fig. 1c), Ag-substrate can slightly improve the performance for site 1 ($|\Delta G|=0.11$ eV changing to 0.08 eV) and worsen site 3 ($|\Delta G|=0.02$ eV to 0.10 eV), but remarkably improve site 2 ($|\Delta G|=0.95$ eV to 0.22 eV) (see Table S2).

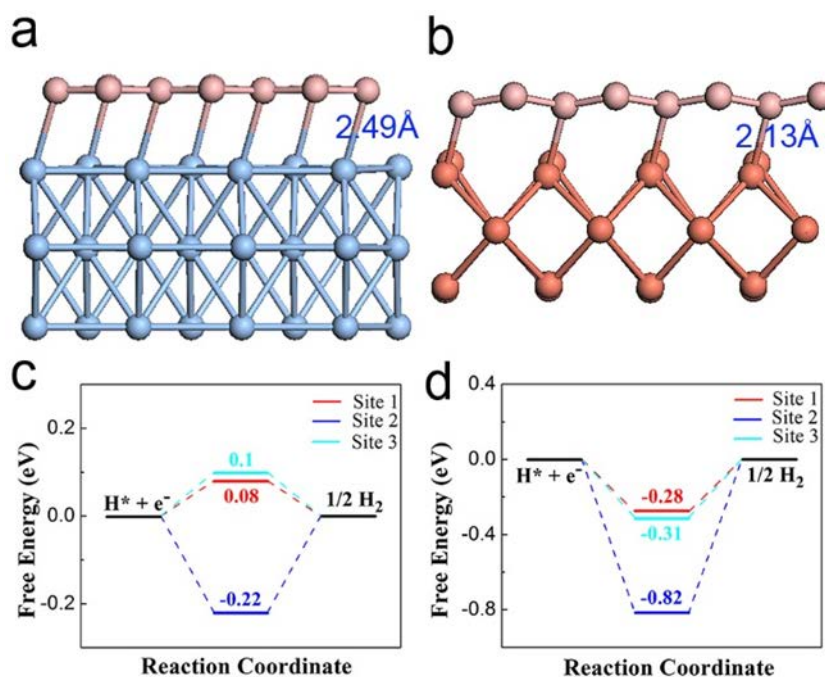


Figure 2. Effect of metal substrate. Optimized geometries of β_{12} sheet on (a) Ag(111) and (b) Cu(111), and calculated ΔG_{H^*} for (c) β_{12} -Ag(111) and (d) β_{12} -Cu(111).

The above results indicate that Ag(111) substrate does not bring negative effect on the HER performance for boron sheet. In the Fig. 2d, we can find that all activity sites of boron sheet were

deteriorated when the β_{12} sheet grows on Cu(111), and all the free energy is change from positive to negative value, indicating stronger interaction between hydrogen and boron. This should be related to the strong electron coupling between boron sheet and metals as strong electron transfer from metals to boron sheet will strengthen H-adsorption, increasing the difficulty for H_2 release and thus resulting higher HER overpotential. Therefore, transferring boron sheets to proper substrate (like Ag) may be an option to further optimize their HER performance.

Now we turn to the investigation of the durability of those active sites. One of the key issues is whether the calculated performance will lose if more hydrogen atoms are introduced to the sheet. Fig. 3 shows the calculated ΔG_{H^*} versus the H-coverages (see Table S3) in the absence of water and a bias potential. And the adsorption geometries at different H-coverages were provided in Supporting Information (see Fig. S1 and S2). As revealed by the calculated ΔG_{H^*} , both α and β_{12} still show excellent HER performance at all these coverages with a maximum value of $\Delta G_{H^*}=0.14$ eV for α and 0.17 eV for β_{12} , being close to MoS_2 -edges.¹¹

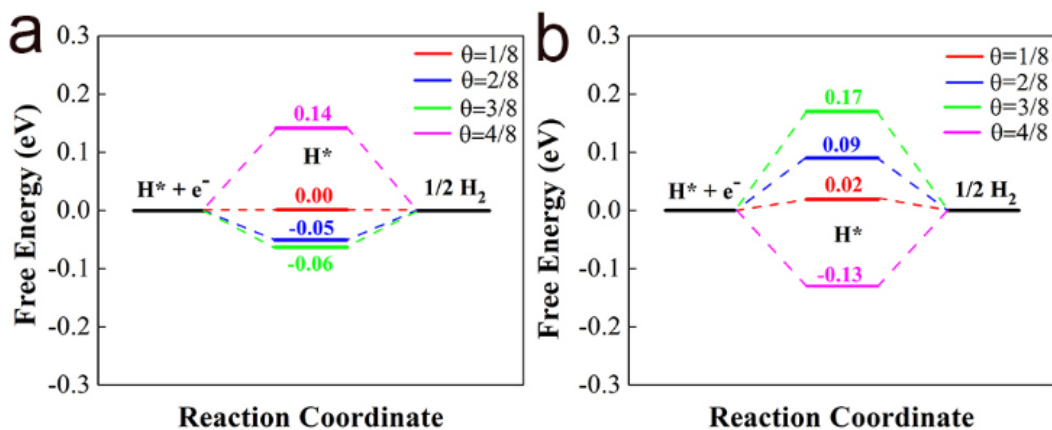


Figure 3. Free energy diagram for hydrogen evolution over two boron sheets: (a) site 1 of α -sheet, (b) site 3 of β_{12} sheet.

To verify the calculated HER activity of two boron sheets, we have cited the data that were carefully selected from the representative literature for several benchmark catalysts, including Pt,⁵ MoS₂ S-edge,¹¹ and Co-MOF.¹⁴ The volcano plot was made using the average Gibbs free energy of hydrogen atoms adsorbed on boron sheet surface as the same hydrogen coverages ($\theta = 1/4$) as the above work in the Fig. 4. And the theoretical exchange current i_0 was calculated using averaged ΔG_{H^*} , labelled as $\Delta G_{H^*}^a$. In this curve, the position of $\log i_0$ and $\Delta G_{H^*}^a$ in the volcano plot are usually used for the evaluation of HER performance. More specifically, the closer to curve peak, the better catalytic activity on the boron sheet.⁹ From Fig. 4, we can find that the value of Pt is located in the left leg of volcano curve, while several 2D materials are located in the right leg of plot. And the value of $\Delta G_{H^*}^a$ and $\log i_0$ of Pt are -0.09 eV and -2.61 A/cm², respectively. While relatively large positive $\Delta G_{H^*}^a$ of Co-MOF and MoS₂ have the comparatively low exchange current which are -2.45 and -3.44 A/cm², respectively. In our work, the positions of two boron sheets are closer to the peak than the Pt, Co-MOF and MoS₂, indicating that they can offer higher exchange current which is favorable for the hydrogen adsorption and release in the HER. Specifically, the calculated $\Delta G_{H^*}^a$ and $\log i_0$ of β_{12} sheet are 0.04 eV and -1.79 A/cm², respectively. While α -sheet even performs better, with $\Delta G_{H^*}^a \sim 0.00$ eV (exactly 0.0023 eV) and $\log i_0 = -1.41$ A/cm², respectively. Therefore, the two boron sheets display the excellent HER performance according to our results, especially for α -sheet.

As HER catalysts need to collect electrons from the electrode and simultaneously attract proton from the solution to generate H*, the coexistence of unpaired electrons and empty states is believed to be beneficial for HER.³⁴ Unsaturated boron (site-1 in α and site-1&3 in β_{12}) along the hole of boron sheets offers such electronic feature, which can also explain the poor performance of site-2 in these sheets. It is also worth to point out that those active sites are stable as evidenced by the

high cohesive energy. In addition, B-sheets present high density of such active sites, with atomic ratio as high as 3/4 and 4/5 for α and site-1&3 in β_{12} , respectively, which is hardly obtainable for MoS₂ and MOF. Currently, the synthesis of boron sheets needs the mediation of metal support, like Cu, Ag and Au.³⁵ As presented in Fig. 2, Ag-substrate can promote HER performance of boron sheet, while Cu-substrate may deteriorate it, indicating a potential approach to further optimize the performance through properly choosing the substrate.

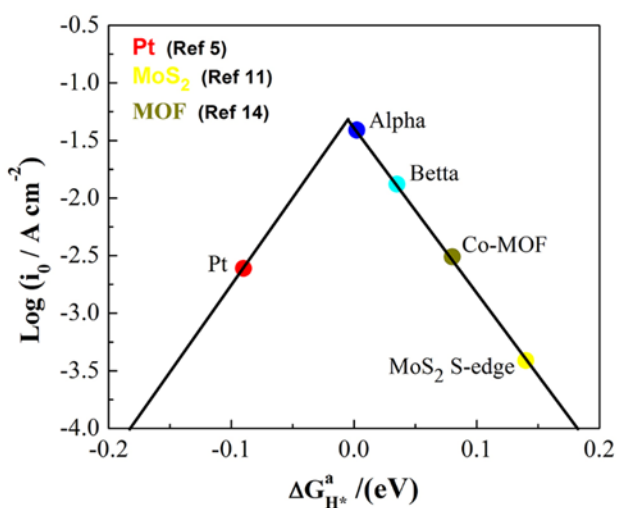


Figure 4. Volcano curve of exchange current (i_0) as a function of the average Gibbs free energy of hydrogen adsorption ($\Delta G_{H^*}^a$).

In summary, HER performance of α and β_{12} sheet has been explored by DFT calculations. As indicated by $\Delta G_{H^*}^a$, both α and β_{12} sheets offer ultralow overpotential for HER and such performance can keep well at different H-coverages. Due to the coexistence of unpaired electron and empty states, unsaturated boron atoms along the hexagon holes are the active sites, with loading as high as 3/4 and 4/5 in terms of atomic ratio. Given boron nanosheets are excellent conductor, metal-free and have been synthesized readily, they are promising candidates for HER.

ASSOCIATED CONTENT

Supporting Information.

The Supporting Information is available free of charge on the ACS Publication website at DOI:

Supporting information file contains:

Computational details (PDF)

Optimized structures (PDF)

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Notes

The authors declare no competing financial interests.

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