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RESEARCH ARTICLE

Enhancing hydrogen evolution of MoS_2 basal planes by combining single-boron catalyst and compressive strain

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MoS_2 is a promising candidate for hydrogen evolution reaction (HER), while its active sites are mainly distributed on the edge sites rather than the basal plane sites. Herein, a strategy to overcome the inertness of the MoS_2 basal surface and achieve high HER activity by combining single-boron catalyst and compressive strain was reported through density functional theory (DFT) computations. The *ab initio* molecular dynamics (AIMD) simulation on B@MoS_2 suggests high thermodynamic and kinetic stability. We found that the rather strong adsorption of hydrogen by B@MoS_2 can be alleviated by stress engineering. The optimal stress of −7% can achieve a nearly zero value of ΔG_H (~ −0.084 eV), which is close to that of the ideal Pt–SACs for HER. The novel HER activity is attributed to (i) the B–doping brings the active site to the basal plane of MoS_2 and reduces the band-gap, thereby increasing the conductivity; (ii) the compressive stress regulates the number of charge transfer between (H)–(B)–(MoS_2), weakening the adsorption energy of hydrogen on B@MoS_2. Moreover, we constructed a SiN/B@MoS_2 heterojunction, which introduces an 8.6% compressive stress for B@MoS_2 and yields an ideal ΔG_H. This work provides an effective means to achieve high intrinsic HER activity for MoS_2.

Keywords MoS_2, stress engineering, single-atom catalyst, HER, charge transfer, DFT, heterojunctions

1 Introduction

With the increasing depletion of fossil fuels and the deterioration of the atmospheric environment, the production of hydrogen fuel through environment-friendly electrochemical and solar-driven photoelectrochemical (PEC) water splitting has become a promising pathway to achieve sustainable energy development [1–7]. The water-splitting reaction ($H_2O \rightarrow H_2 + 1/2O_2$) is divided into two half-reactions: the oxygen evolution reaction (OER) and the hydrogen evolution reaction (HER), which occur on the anode and cathode, respectively [1, 8]. Taking HER as an example, the mechanism of reaction in an acidic environment involves three steps: (i) Generating an adsorbed hydrogen atom on the cathode (the Volmer or discharge reaction: $H^+ + e^- + * \rightarrow H^*$); (ii) the combination of two adsorbed hydrogen to produce H_2 (the Tafel reaction: $2H^* \rightarrow H_2 + 2*$); (iii) another electron reacts with the adsorbed hydrogen and another proton in the solution to form H_2 (the Heyrovsky reaction: $H^* + H^+ + e^- \rightarrow H_2 + *$) [8–11]. The high activation energies required to form the reaction intermediates on the cathode surface will inevitably create the large kinetic barriers [12]. The resulting overpotential (the potential difference between theoretical thermodynamic potential and the experimental potential) required to drive the reaction has a significant effect on HER performance and must be taken into account [13]. Therefore, how to effectively reduce the overpotential to the greatest extent has become the most critical issue for the commercialization of the HER.

Fortunately, numerous related reports have shown that the introduction of suitable catalysts can decrease the overpotential and speed HER up, maximizing the energy conversion efficiencies [14–27]. As a traditional indus-

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trial hydrodesulfurization catalyst, MoS_2 has attracted widespread attention in recent years because of its performance tunability, low cost, and good stability [28–33]. MoS_2 has three common structures, 1T-, 3R-, and 2H-MoS_2. Among them, the semiconductor 2H–MoS_2 has the best thermodynamic stability [1, 34], which will be hereinafter referred to as MoS_2. Previous studies have shown that the basal plane of MoS_2 is usually inert for H adsorption, and only a few active sites are distributed on the edge [35, 36]. Therefore, these defects should be overcome before the large-scale application of MoS_2. So far, the initial MoS_2 optimization can be divided into two directions, one strategy to change MoS_2 monolayer nanostructures, such as vertical nanoflake [37], nanoparticles [38], nanowires [39], mesoporous films [40] or defect-rich films [41], maximum exposure edge active sites, another strategy to enhance intrinsic activity of the edge sites by atomic scale modifications, such as construction defects [36, 40] and chemical doping at edge sites [42]. Note that the basal planes constitute the vast majority of bulk materials [36]. A strategy to activate the basal plane is beneficial for maximizing the commercialization of MoS_2. Unfortunately, the relevant research is not complete.

Recently, single-atom catalysts (SACs) become a rising star in the field of catalysts, which perfectly inherit the advantages of both heterogeneous and homogeneous catalysts [43–45]. The extreme atomic utilization efficiency enables SACs to exhibit excellent catalytic performance even under low loss conditions, which is conducive to achieving the atomic economy [46]. Secondly, the active center sites of SACs are completely exposed [47]. The charge transfer effect between the active center atom and the substrate and their low coordination environment ensures the activity of SACs in various reactions [48–50]. In addition, structural simplicity facilitates precise characterization, which, in turn, helps to achieve rational SACs design at the atomic scale [44, 51]. Importantly, we noticed that MoS_2 with stable physicochemical properties is suitable as a substrate for SACs to avoid single-atom agglomeration [52]. Currently, the vast majority of SACs that have been developed are transition metal-based, such as Pt SACs [53, 54], Ru SACs [55, 56], Mo SACs [57, 58], Cu SACs [59, 60], Fe SACs [61, 62], Co SACs [63, 64] and our previous study on V SACs [52]. However, the deficiency of metal SACs including low selectivity, low faradaic efficiency, low production rate, and excessive dependence on pH must be overcome before they are widely used [65, 66]. Fortunately, Braunschweig *et al.* pioneered a new strategy for N_2 fixation based on metal-free center in 2018 [67]. However, to our knowledge, only a few metal-free SACs have been reported, such as single-boron catalyzed N_2 reduction reaction (NRR) [68–70], and single-iodine catalyzed HER [71]. Therefore, the exploitation of highly efficient metal-free SACs and their application in electrocatalytic HER will become a research hotspot in this field. Importantly, Liu *et al.* [72] emphasized that the single boron atom catalysts (B SAC) embedded in the defective MoS_2 monolayer with S vacancies may be more inclined to promote HER in their study on the SACs for NRR.

In addition, strain engineering has been proven to be a powerful strategy for regulating the electronic structure of the two-dimensional (2D) nanomaterial and optimizing the catalytic performance in recent years [73–76], which can restore the hope of many initially unpromising catalysts [77–83]. As early as 1998, Mavrikakis *et al.* [84] regulated the surface electron structure and the energy of reaction intermediates by adjusting the surface strain. Since then, many researchers have focused on adjusting surface stress to improve catalyst efficiency [82, 85–89]. Regarding a famous case of oxygen reduction reaction (ORR) on platinum, previous studies have shown that a 1% compressive strain can increase its activity by more than 300% [82, 86]. Importantly, Li *et al.* [36] pointed out in their work on activation and optimization of monolayer MoS_2 for HER by introducing S vacancies and strain that appropriate strain can significantly improve the properties of MoS_2 for HER. Similarly, Pan *et al.* [90] successfully adjusted the electronic and magnetic properties of MoS_2 nanoribbons with strain engineering, and predicted the potential applications to spintronics and photovoltaic cells.

In this work, we successfully reported for the first time a strategy to achieve high HER activity of MoS_2 basal planes by combining strain and B SAC through density functional theory (DFT) calculations. The *ab* initio molecular dynamics (AIMD) simulation on B@MoS_2 (single boron atom embedded in MoS_2 basal plane) suggests high thermodynamic stability. Through applying tunable stress, the optimal stress to obtain ideal hydrogen adsorption free energy (ΔG_H) was determined. The underlying mechanism for the novel HER performance was explored. Moreover, the IV–V/B@MoS_2heterojunction (heterojunction of the group IV–V compounds and B@MoS_2) was constructed to simulate the effect of compressive stress on the HER performance of B@MoS_2. The methodology of combining SACs and stress could be a general strategy of optimizing catalytic performance for materials beyond MoS_2.

2 Calculation methods

Our DFT calculations were performed using the generalized gradient approximation of the Perdew–Burke–Ernzerhof functional (GGA/PBE), implemented in the Vienna Ab Initio Simulation Package (VASP) [91–93]. The projector augmented wave (PAW) [91] potential was used to describe the ion-electron interactions with the valence state $2s$ and $2p$ for B, $3s$ and $3p$ for S, $4d$ and $5s$ for Mo, respectively. The thickness of the vacuum layer was fixed at 15 Å in the z-direction to prevent peri-

odic layer-to-layer interactions. A Γ-centered 3×3×1 (geometry optimization) and 5×5×1 (self-consistent energy) Monkhorst–Pack grids for the Brillouin zone sampling and cutoff energy of 500 eV for plane wave expansion were used in the calculations. In the geometry optimization, all atoms were allowed to relax in the cell until the maximal residual force and energy on each atom was less than 0.01 eV/Å and 1.0×10^{-4} eV/atom, respectively. The long-range van der Waals (vdW) interaction often has a great influence on the structure of 2D materials [94], MoS_2 being one of them [17]. In this work, Grimme's scheme (D3) [95] was used to modify the long-range dispersion interactions.

The binding energy of the B atom (E_b(B)) embedding (substitution or adsorption) on MoS_2 was calculated by the following equation:

$$E_{\mathrm{b}}(\mathrm{B}) = E_{\mathrm{B@MoS_2}} - (E_{\mathrm{MoS_2}} + E_{\mathrm{B}} - nE_{\mathrm{S}}), \quad (1)$$

where $E_{\mathrm{B@MoS_2}}$ and $E_{\mathrm{MoS_2}}$ are the total self-consistent energy of the B@MoS_2, MoS_2. E_{B} and E_{S} are the cohesive energy of the B and S atoms [96, 97]. $n = 1$ if B atom substitutes for S atom, otherwise $n = 0$. In general, the negative E_b(B) corresponds to a stable catalyst system.

Regardless of the acid solubility and alkalinity of the reaction, the overpotential of the HER is always determined by the Gibbs free energy change of the Volmer reaction ($H^+ + e^- + * \rightarrow H^*$) [8, 46]. Thus, the absolute value of ΔG_{H} is the energy barrier to be overcome for the HER [8, 98, 99]. ΔG_{H} is calculated by the following equation:

$$\Delta G_{\mathrm{H}} = \left[E_{\mathrm{H}*} + E_{\mathrm{ZPE(H}*)} - TS_{(\mathrm{H}*)}\right] - E_{(*)} - \frac{1}{2}\left[E_{(\mathrm{H_2})} + E_{\mathrm{ZPE(H_2)}} - TS_{(\mathrm{H_2})}\right], \quad (2)$$

where $E_{\mathrm{H}*}$, $E_{(*)}$ and $E_{(\mathrm{H_2})}$ are the total self-consistent energy of the H* (B@MoS_2 adsorbs one proton), * (B@MoS_2), and free H_2 molecule, respectively. E_{ZPE} and S are the zero-point energy (ZPE) and entropy, respectively. According to the method developed by Norskov and colleagues [100, 101], the free energy of ($H^+ + e^-$) has been replaced by half the chemical potential of a hydrogen molecule. For H_2, ZPE, and S can be obtained from NIST-JANAF thermochemical tables [102]. It should be noted here that the pH is assumed to be zero, which means

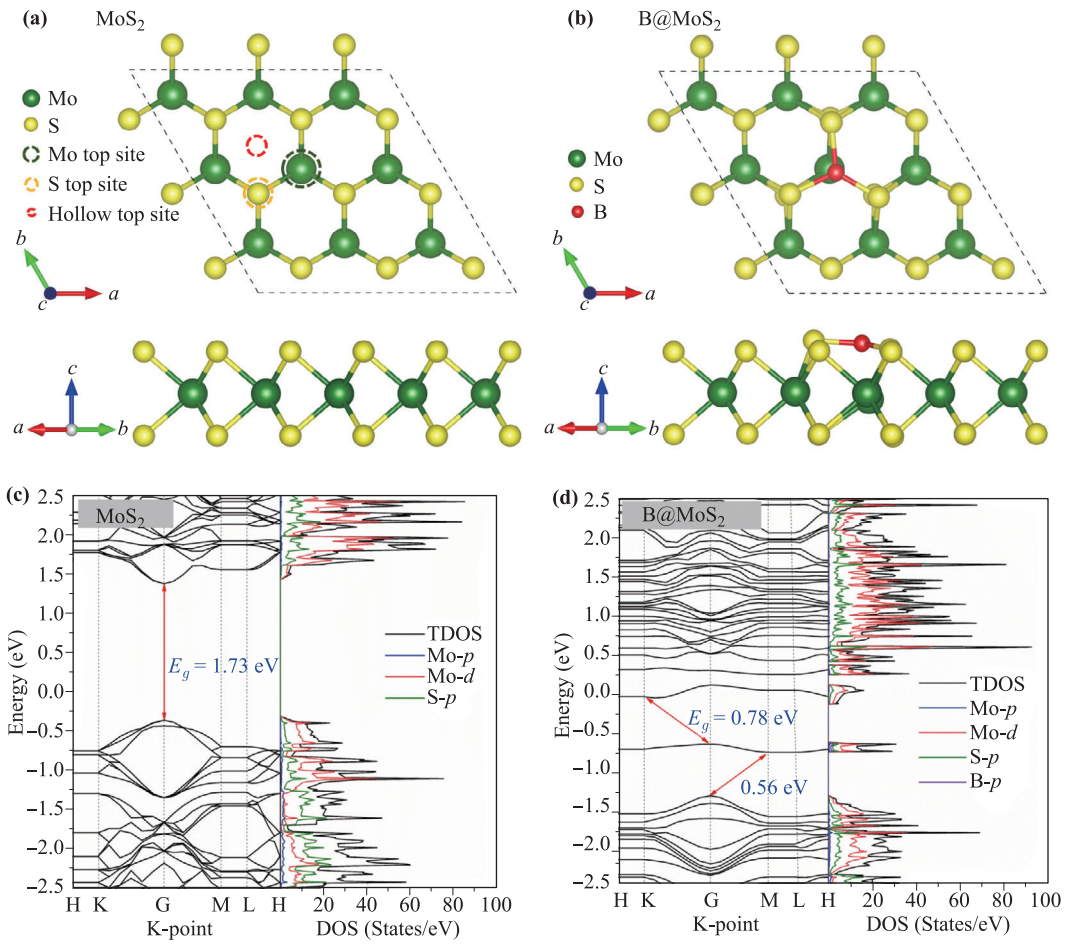


Fig. 1 The optimized structure (top and side views) and the calculated band structure and DOS of the 3 × 3 × 1 MoS_2 **(a, c)** and B@MoS_2 **(b, d)** supercell. The top view of (a) shows the sites where the B atom may be embedded (adsorbed or replaced), i.e., the Mo top site, the S top site, the hollow top site, and replacing the S atom. The Fermi level is set to zero.

the relationship between the overpotential and the pH is ignored in this work. According to the Sabatier principle, the ΔG_{H} of an ideal catalyst should be infinitely close to zero, where hydrogen is bound neither too strongly nor too weakly [103].

In addition, if the ZPE and entropy are not included in the Eq. (2), we can also obtain the adsorption energy of H^+ ($E_{ads}(H^+)$) on the surface of B@MoS_2 by the following equation:

$$E_{ads}\left(\mathrm{H}^+\right) = E_{\mathrm{H}*} - E_{(*)} - \frac{1}{2}E_{(\mathrm{H}_2)}. \tag{3}$$

3 Results and discussion

3.1 Stability and electronic structure of B@MoS_2

Based on other similar studies [104, 105], we constructed a $3 \times 3 \times 1$ MoS_2 supercell, including 9 Mo and 18 S atoms, and optimized by GGA/PBE + D3 method which has been proved to accurately describe the geometry and electronic structure of MoS_2 [42], as shown in Fig. 1(a). Note that we also have carried out a similar study on a $4 \times 4 \times 1$ MoS_2 supercell, and obtained consistent structural parameters and E_b(B), proving that $3 \times 3 \times 1$ MoS_2 supercell is large enough. The lattice parameter of the primitive MoS_2 is 3.168 Å, the thickness of the monolayer is 3.2 Å, and the bond length of Mo–S bond is about 2.41 Å, which are in good agreement with the experimental report [106] and other theoretical studies [97, 107–109]. High stability is a precondition for catalysts. Strong bonding between the substrate and the supported atom is necessary to avoid the aggregation of the single atom. For the embedded B atom, we considered four typical structures, including a B atom substituting one S atom and a B atom adsorbed on top of Mo atom, S atom, and vacancy, as shown by the circle in Fig. 1(a). The most stable B@MoS_2 structure with the lowest E_b(B) of −1.607 eV is obtained, as shown in Fig. 1(b). A negative E_b(B) means that the B atom on the B@MoS_2 surface is energetically more stable than that in the bulk form [52]. The other three metastable structures and E_b(B)s are summarized in Fig. S1. Therefore, the following B@MoS_2 refers specifically to the structure of B atom adsorbing on top of Mo atom Fig. 1(b). Furthermore, the AIMD simulations on at 300 K for 10 ps with a time step of 2 fs is performed to check the thermal stability of B@MoS_2 structures [69, 96]. As shown in Fig. 2, no obvious geometry buckling of B@MoS_2 was observed during the AIMD simulations. Therefore, B@MoS_2 is thermodynamically stable.

The calculated band structure and the DOS (total density of states (TDOS) and partial density of states (PDOS)) of MoS_2 and B@MoS_2 are shown in Fig. 1(c) and Fig. 1(d), respectively. The MoS_2 behaves as a direct gap semiconductor with the band-gap energy (E_g) of 1.73 eV, which is close to the theoretical result obtained by Pan *et al.* (1.72 eV) [90]. The B-doping introduces an impurity level in the forbidden gap, which provides a new platform for electronic transitions and improves the conductivity of the catalyst. Both the conduction band minimum (CBM) and the valence band maximum (VBM) of MoS_2 and B@MoS_2 are mainly contributed by Mo-d and S-p orbitals, of which the Mo-d is the main component. The impurity states near the center of the forbidden band of B@MoS_2 are generated by the hybridization of B-p orbitals and Mo-d orbitals, as seen in Fig. 1(d) and Fig. 4(c).

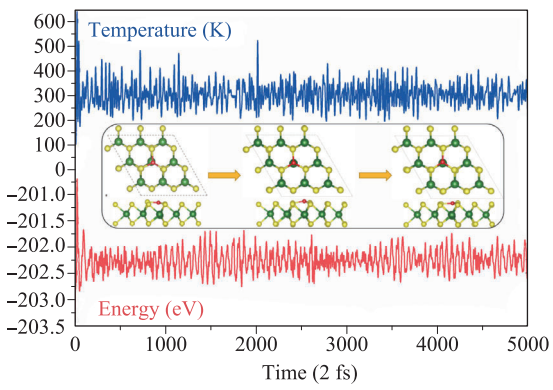


Fig. 2 The temperature and energy curve with time, in AIMD simulations for 10 ps under 300 K with a time step of 2 fs. The insert figures are the initial, intermediate, and final structure of B@MoS_2 (top and side views).

3.2 The ΔG_{H} of B@MoS_2 under stress activation and optimization

The dispersed B atoms as active sites make the inert basal plane of MoS_2 active for H^+ adsorption. According to Eq. (2), the ΔG_{H} of B@MoS_2 is calculated to be −0.451 eV, which is far from the ideal value of zero. Interestingly, previous studies showed that the process of adsorbing H^+ on the surface of MoS_2 is an endothermic reaction [36], which is converted into an exothermic spontaneous reaction after doping with B atoms (refer to Fig. S3). The loading of B SAC on MoS_2 makes it a strong absorbent for H^+, leading to the large barrier for H_2 release. We note that the electronic structure of 2D materials is sensitive to strain [13]. So, it is productive to adjust its adsorption ability towards adsorbates by strain engineering. In this work, we attempt to use this method to weaken the adsorption ability of B@MoS_2 for H^+ to activate and optimize the capacity of B@MoS_2 for HER.

The biaxially adjustable stress is simulated by changing the lattice size of the B@MoS_2, as shown in Fig. 3(a). According to the direction of stress, the strain can be divided into tensile strain and compressive strain. The stress magnitude is determined by the following equation:

$$\varepsilon = \left(\frac{L - L_0}{L_0}\right) \times 100\%, \tag{4}$$

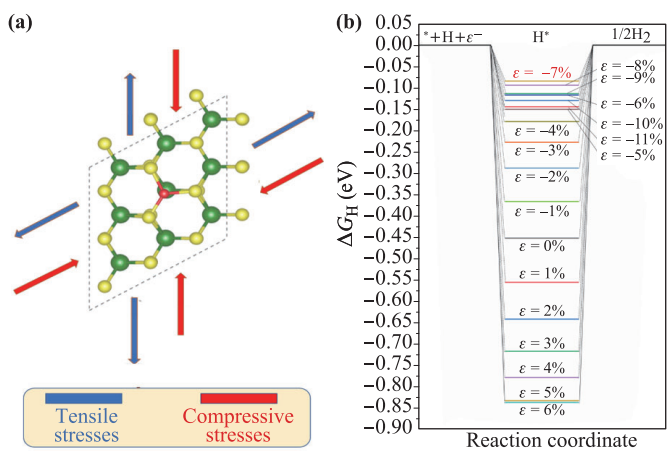


Fig. 3 **(a)** Schematic diagram of applying tunable strain to B@MoS_2. **(b)** The ΔG_H diagrams of B@MoS_2 for HER under tunable strain ($-11\% \leq \varepsilon \leq 6\%$). **(c)** The ΔG_H trend diagram with the tunable strain ($-11\% \leq \varepsilon \leq 6\%$).

where L_0 and L are the calculated supercell sizes before and after the stress application, respectively [90]. Therefore, ε is positive for tensile stress, whereas negative for compressive stress.

Since there are very stable atomic bonds in the 2D MoS_2 plane, the breaking strength is up to 18 $N{\cdot}m^{-1}$, which can sustain 11% elastic strain [110, 111]. Therefore, within the tolerable range of MoS_2, we investigated the ΔG_H under tunable strain ($-11\% \leq \varepsilon \leq 6\%$), and the result is shown in Figs. 3(b) and (c). The lattice parameter and ΔG_H data of B@MoS_2 under different stress are summarized in Tables S1 and S2. In the range of the applied strain, the adsorption of H^+ is always the spontaneous exothermic process, indicating the strong adsorption capability of B@MoS_2 for H^+. As the compressive stress increases, the adsorption capacity of B@MoS_2 for H^+ gradually decreases until $\varepsilon = -7\%$. We see that the ΔG_H corresponding to $\varepsilon = -7\%$ is closest to zero, about -0.084 eV, which is very close to that of the ideal Pt–SACs for HER (~ -0.07 eV) [53, 54]. On the contrary, as the tensile stress increases, the adsorption capacity of B@MoS_2 for H^+ continues to increase until saturation ($\varepsilon = 5\%$). Therefore, $\varepsilon = -7\%$ is the most suitable stress for B@MoS_2 to catalyze HER. In the strained B@MoS_2 with $\varepsilon = -7\%$ (-7% B@MoS_2), the Mo–S bonds are shortened under the compressive stress, but the reduction is only about 1.66%, indicating that the B@MoS_2 keeps the lattice structures [90]. In addition, the E_b(B)of -7% B@MoS_2 is determined to be -2.24 eV, which means that the -7% B@MoS_2 has certain structural stability while having the best catalytic performance.

3.3 Origins of the high HER activity on -7% B@MoS_2

We further discuss the origin of high hydrogen desorption activity of B@MoS_2 under proper compressive stress. The band structure and DOS of -7% B@MoS_2 were calculated, as shown in Fig. 4(a). The E_g of B@MoS_2 is further reduced under the action of compressive stress. The CBM and VBM are still mainly contributed by the Mo-d and S-p orbitals. Comparing Fig. 4(c) and Fig. 4(d), the contribution of B-p orbitals to the hybridization of Mo-d and B-p orbitals further increases in range of -0.75–-0.5 eV. At the same time, it is interesting that the extraneous B atom moves the Fermi energy level into the conduction band, greatly improving the conductivity of the original MoS_2, and ensuring the effective transfer of electrons in the HER process.

To associate the ΔG_H with the interaction between the substrate and adsorbed hydrogen, we illustrate the stress-dependent $E_{ads}(H^+)$ by Eq. (3) in Fig. S2. Obviously, $E_{ads}(H^+)$ and ΔG_H have the same trend with the applied stress. The $\varepsilon = -7\%$ corresponds to the weakest adsorption for H. One knows that $E_{ads}(H^+)$ is closely related to the charge transfer between the adsorbed hydrogen and the substrate. The charge density differences of B@MoS_2 and -7% B@MoS_2 before and after adsorbed hydrogen are shown in Fig. 5. Positive (electron deficit) and negative (electron excess) lobes are shown in light-blue and crimson isosurfaces, respectively. It is clear that charge redistribution occurs between the adsorbed hydrogen, fixed B atom, and MoS_2. According to the calculation results of Bader charge transfer (Table S3), we draw a schematic diagram of the charge transfer path under special stress ($\varepsilon = 0$, -7%, -11%), as shown in Fig. 6. We represent the number of transferred electrons by the red number. For all the models, B atom donates electrons to the adsorbed hydrogen and the substrate simultaneously. Compared with the stress-free B@MoS_2, the -7% compressive stress enhances the Mo-d and B-p hybridization. So, the charge transfer between B and MoS_2 rapidly increases from $0.592e$ to $1.01e$, and the electrons obtained by adsorbed hydrogen decreases from $0.533e$ to $0.346e$, leading to the weakened adsorption for H^+ (Fig. S2). However, as the compressive stress increases continually ($\varepsilon > -7\%$), we find that the charge transfer between B atom and MoS_2 is basically unchanged, suggesting the hybridization saturates. At the same time, the charge exchange between adsorbed hydrogen and B atom increases, and the $E_{ads}(H^+)$ is enhanced. The effect of stress on the d orbitals of the metal atom can explain this phenomenon. In general, the sp bands of

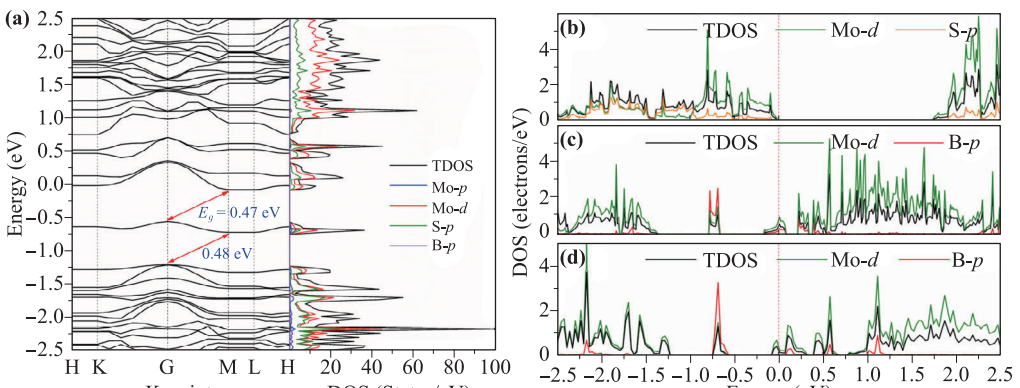


Fig. 4 **(a)** Calculated band structure and DOS of −7% B@MoS_2. The simplified DOS of MoS_2 **(b)**, B@MoS_2 **(c)**, and −7% B@MoS_2 **(d)**. Note that herein we average the DOS to each corresponding atom to get the figure. The Fermi level is set to zero.

metal are broad and structureless, while the d-band are narrow. The interaction between *d* states and adsorbate states can be significantly changed by even small stress changes. The compressive strain causes the Mo-*d* orbitals to overlap, reducing the d-band center energy [74]. Therefore, more unoccupied antibonding states are pushed below the Fermi level, allowing B to interact with them, and promoting charge transfer between B and MoS_2 [74, 112].

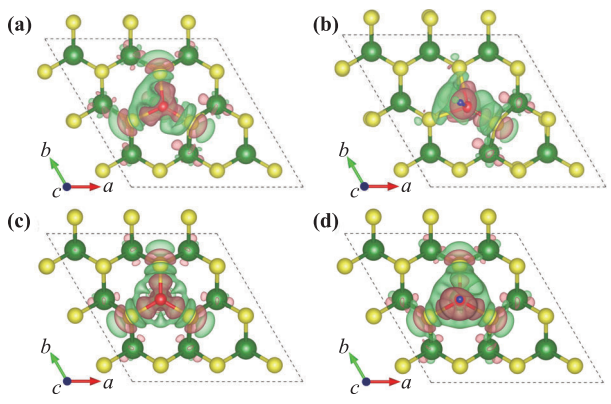


Fig. 5 The top views of the three-dimensional charge density difference plots for B@MoS_2 **(a)** and −7% B@MoS_2 **(b)**, and H^+ adsorbed B@MoS_2 **(c)** and −7% B@MoS_2 **(d)** with an isovalue of 0.004 e/Å^3. Positive (electron deficit) and negative (electron excess) lobes are shown in light-blue and crimson isosurfaces, respectively.

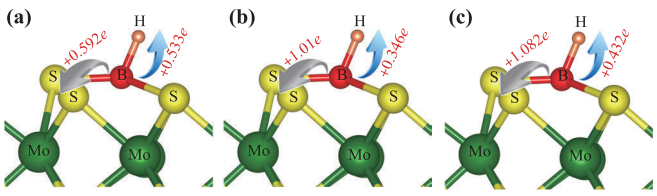


Fig. 6 Schematic diagram of the charge transfer path under $\varepsilon = 0\%$ **(a)**, $\varepsilon = -7\%$ **(b)**, and $\varepsilon = -11\%$ **(c)**. The blue and gray arrows indicate the transfer of electrons from the B atom to the adsorbed H and substrate, respectively. The "+*" denotes gaining electrons number form B atom.

When the overlap of Mo-*d* orbitals reaches saturation, this promotion is interrupted. Thus, the charge transfer between B atom and adsorbed hydrogen is restored.

3.4 The realization of suitable stress

The current mainstream stress realization method can be summarized as manufacturing lattice mismatch, such as generating strain through lattice mismatches of 2D material heterojunction or homojunction [13]. The idea of using the unique electronic structure of the heterojunction to reduce the overpotential of the HER has been verified by a large number of studies [113–116]. Typically, Singh *et al.* [115] carried out a study on graphene-supported TiO_2 to promote carrier photocatalytic water splitting, and the ultrathin $MoSe_2$ nanosheets coated on hollow carbon spheres synthesized by Yuan *et al.* [116] was used as high-efficiency catalysts for HER, etc. Inspired by depositing a monolayer MoS_2 grown by chemical vapor deposition (CVD) on a SiO_2 substrate with microcavities [117], we envision the growth of MoS_2 on a 2D material surface with a suitable lattice parameter. In this section, two monolayer group IV–V compounds (SiN and GeN) are examined as substrates, which have slightly smaller lattice parameters than that of B@ MoS_2 (SiN: 2.895 Å, GeN: 3.091 Å) and high theoretical stability [118]. As shown in Fig. 7, the IV–V/B@MoS_2 nano-heterojunction (GeN/B@MoS_2 and SiN/B@MoS_2) are constructed, which include 4 × 4 IV–V supercell and 4 × 4 B@MoS_2 supercell.

After full relaxation, the equilibrium distance between the IV–V layer and the B@MoS_2 layer is 3.5 Å, and the cross-sectional dimensions of two heterojunction supercells are 12.364 Å × 12.364 Å (GeN/B@MoS_2) and 11.580 Å × 11.580 Å (SiN/B@MoS_2), respectively. To evaluate the stability of the IV–V/B@MoS_2 heterojunction, the interface adhesion energy (E_{adh}) is defined according to the following equation:

$$E_{adh} = E_{\text{heter}} - E_{\text{IV-V}} - E_{\text{B@MoS}_2}, \tag{5}$$

where E_{heter}, $E_{\text{IV-V}}$, and $E_{\text{B@MoS}_2}$ are the total self-

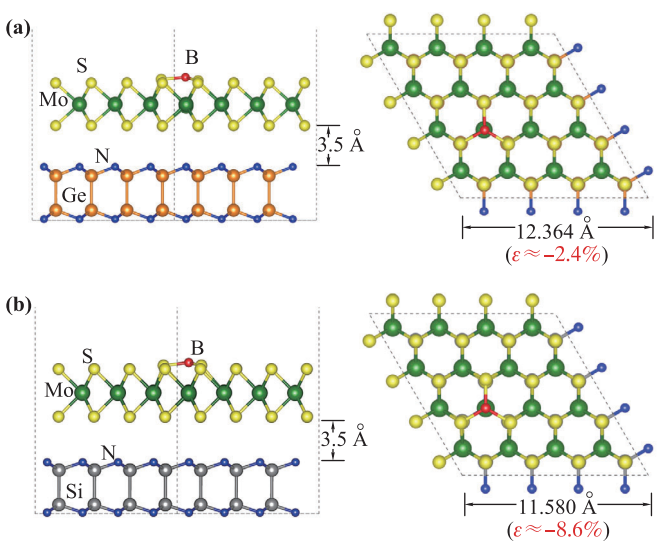


Fig. 7 Optimized GeN/B@MoS_2 **(a)** and SiN/B@MoS_2 **(b)** interface in a side view (left) and top view (right). The balls of different colors correspond to each atom type.

consistent energy of the IV–V/B@MoS_2 heterojunction, the pure IV–V, and the B@MoS_2 monolayer, respectively. The E_{adh} of IV–V/B@MoS_2 is as low as −3.376 eV (GeN/B@MoS_2) and −3.262 eV (SiN/B@MoS_2), respectively, which are stronger than the known GaS/GaSe (−1.947 eV) and graphene/MoS_2 (−0.023 eV) [119, 120]. Therefore, GeN/B@MoS_2 and SiN/B@MoS_2 are considered feasible. According to Eq. (4), the GeN/B@MoS_2 heterojunction is equivalent to applying a 2.4% compressive stress to B@MoS_2 and yields a ΔG_H of −0.281 eV, which is close to the predicted value in Fig. 3(c). Excitingly, the SiN/B@MoS_2 heterojunction is equivalent to apply an 8.6 % compressive stress to B@MoS_2 and gives a ΔG_H of −0.098 eV. It provides a theoretical basis for B@MoS_2 as an alternative to precious metal Pt–SACs for HER.

4 Conclusions

In summary, based on DFT and AIMD calculations, we designed a stable metal-free B SAC on MoS_2 (B@MoS_2) for HER. The anchored B atoms make the MoS_2 basal surface to be active for H adsorption. By optimizing stress, a compressive stress of −7% can achieve a nearly zero value of ΔG_H, about −0.084 eV, which is close to that of the ideal Pt–SACs for HER. The compressive stress regulates the number of charge transfer between (H)–(B)–(MoS_2), weakening the $E_{ads}(H^+)$ on the surface of B@MoS_2. Moreover, B doping and compressive stress reduce the bandgap and move the Fermi energy level to the conduction band, improving the conductivity of the pristine MoS_2. Finally, the SiN/B@MoS_2 heterojunction with a −8.6% compressive stress to B@MoS_2 is found to give a ΔG_H of −0.098 eV. This work not only provides an effective strategy for improving the catalytic activity of MoS_2 for HER, but also inspires more researchers to further explore and optimize the potential of metal-free SACs for HERs.

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Supporting Information

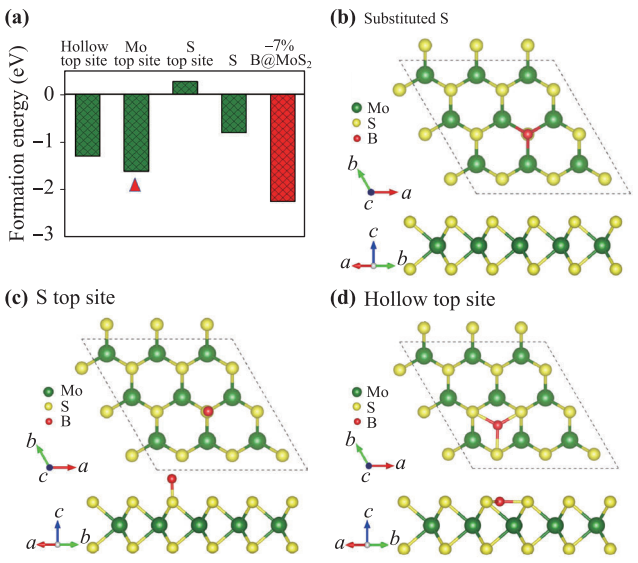


Fig. S1 **(a)** The E_b(B) of four possible structures of B@MoS_2. The top (top) and side views (bottom) of B@MoS_2 optimized structure with B atom replacing S atom **(d)** and adsorbed on the top of the vacancy **(b)**, S atoms **(c)**, respectively.

Fig. S2 The $E_{ads}(H^+)$ trend diagram with strain-tunable ($-11\% \leq \varepsilon \leq 6\%$). The red data points correspond to the three special stresses considered in Table S2.

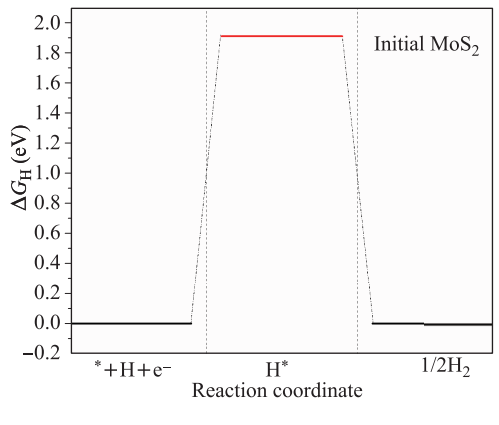


Fig. S3 Gibbs free energy diagrams of the HER on initial MoS_2 basal plane.

Table S1 The δG_H calculation data corresponding to each stress (ε), where "H" is the energy of half H_2 corrected by ZPE. Note that the H already includes the zero-point energy (ZPE) and entropy.

ε	*H	ZPE	TS	*	H	ΔG_H
−11	−195.552	0.257	0.004	−191.7	3.455	−0.144
−10	−197.801	0.256	0.005	−193.965	3.455	−0.129
−9	−199.756	0.256	0.005	−195.937	3.455	−0.113
−8	−201.432	0.256	0.005	−197.632	3.455	−0.094
−7	−202.858	0.256	0.005	−199.067	3.455	−0.084
−6	−204.084	0.256	0.004	−200.26	3.455	−0.117
−5	−205.1	0.256	0.005	−201.243	3.455	−0.15
−4	−205.913	0.256	0.005	−202.028	3.455	−0.179
−3	−206.544	0.257	0.005	−202.609	3.455	−0.227
−2	−207.009	0.257	0.005	−203.015	3.455	−0.288
−1	−207.33	0.257	0.005	−203.256	3.455	−0.366
0	−207.507	0.256	0.005	−203.35	3.455	−0.451
1	−207.547	0.256	0.005	−203.287	3.455	−0.555
2	−207.448	0.255	0.005	−203.103	3.455	−0.641
3	−207.217	0.254	0.006	−202.798	3.455	−0.716
4	−206.86	0.252	0.006	−202.382	3.455	−0.777
5	−206.381	0.251	0.006	−201.85	3.455	−0.831
6	−205.785	0.251	0.006	−201.25	3.455	−0.835

Table S2 The lattice size of the $3\times3\times1$ B@MoS_2 supercell and the corresponding δG_H under stress.

Stress (ε)	a (Å)	δG_H (eV)	Stress (ε)	a (Å)	δG_H (eV)
−11%	2.82	−0.144	−2%	3.105	−0.288
−10%	2.851	−0.129	−1%	3.137	−0.366
−9%	2.883	−0.113	0%	3.168	−0.451
−8%	2.915	−0.094	1%	3.2	−0.555
−7%	2.946	−0.084	2%	3.232	−0.641
−6%	2.978	−0.117	3%	3.263	−0.716
−5%	3.01	−0.15	4%	3.295	−0.777
−4%	3.042	−0.179	5%	3.327	−0.831
−3%	3.073	−0.227	6%	3.358	−0.835

Table S3 The δQ (in e) is the number of transferred electrons under strain-tunable via Bader charge analysis (the "+" or "−" denotes gaining or losing electrons).

ε	δQ (e)		
	MoS_2	B	Adsorbed H
0%	0.592	−1.125	0.533
−7%	1.01	−1.356	0.346
−11%	1.082	−1.514	0.432

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