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# Single-atom transition metals doping two-dimensional $B_xN$ materials ( $X = 2, 3, 5$ ) with promising electrocatalytic activity for efficient hydrogen production in the entire pH range†

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Two-dimensional (2D) boron nitrides (BN) have been eagerly and widely used and have tremendous potential in several advanced fields, such as energy harvesting and storage. Due to their significant electronic properties, they are also commonly used as substrates for single-atom catalysts (SACs). Therefore, with the aid of a computer, we designed SACs by doping isolated single atoms of 3d, 4d, and 5d transition metals (TM) on 2D  $B_xN$  materials ( $X = 2, 3, 5$ ). In addition, pH regulation is considered to improve the electrocatalytic hydrogen evolution reaction (HER) activity, and the materials' effectiveness was investigated theoretically based on density functional theory (DFT) calculations. Our results indicate that the low-cost TM SACs can effectively enhance the HER catalytic performance over a wide range of pH. Among all the SACs studied, Ti-, V-, Y- and Zr@ $B_5N$  show excellent catalytic activity at pH = 0, with the Gibbs free energy change ( $\Delta G_{H^+}$ ) of hydrogen adsorption of  $-0.027$ ,  $-0.094$ ,  $0.073$  and  $-0.040$  eV, respectively. We find that Sc- and Y-embedded  $B_2N$ , Co-, Fe-, and Mo-embedded  $B_3N$  and Co-, Cr-, V-, Ti-, Y-, Zr-, Nb-, Ru-, and Tc-embedded  $B_5N$  SACs have excellent catalytic activity in acidic conditions, while Ir-embedded  $B_5N$  shows high catalytic activity in alkaline conditions. Interestingly, Ti@ $B_2N$ , Mn@ $B_3N$ , Fe@ $B_5N$  and Mo@ $B_5N$  SACs are highly active in either acidic or alkaline environments. Our work opens new avenues for designing cost-effective SACs with wide-pH-range HER performance.

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## 1. Introduction

Hydrogen is considered to become the cleanest energy source in the world due to its advantages such as abundant raw materials, environmental protection, high energy and recyclability.<sup>1–3</sup> Therefore, the development of a safe, efficient and low-cost hydrogen production process is crucial to solve the serious environmental pollution and energy shortage problems. Among them, electrochemical hydrogen evolution reaction (HER) is considered to be the most promising and sustainable industrial hydrogen production method, and the role of catalysts is indispensable.<sup>4–8</sup> At present, the precious

metal platinum is considered to be the best electrocatalyst for HER because of its excellent kinetic and thermodynamic efficiency.<sup>9–13</sup> However, the scarcity and high cost of precious metals are important factors hindering their large-scale and sustainable application, which cannot be ignored.<sup>13–15</sup> Therefore, it is very important to find both efficient and low-cost HER electrocatalysts, which have extremely important significance.

In order to develop a practical HER catalyst—in addition to considering some basic requirements such as the cost, stability and conductivity of the catalyst—it must also have the ability to trigger proton reduction with the minimum overpotential, as well as fast kinetic performance. In recent years, the unique surface structure and electronic properties of two-dimensional (2D) materials have provided new opportunities and challenges in the development of HER catalysts.<sup>16–23</sup> Two-dimensional materials have the advantages of high durability, low cost and excellent environmental protection, and they have unique physical and chemical properties such as stronger surface activity, faster charge transfer and adjustable band gap, which give them broad application potential in the fields of catalysts, sensors and photodetectors.<sup>24–33</sup> So far, 2D HER catalysts based on non-metallic nanomaterials have received a lot of attention.

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The intrinsic catalytic activity of 2D materials and the formation of single atom catalysts (SACs) by deposition of transition metal (TM) atoms on the surface of 2D materials are two new areas of cutting-edge catalytic research, which have revealed new catalytic processes at the atomic scale.<sup>34–36</sup>

In recent studies, various synthesized SACs showed excellent catalytic properties in different reactions.<sup>37–40</sup> In order to meet the basic requirements of efficient SAC substrate materials, it is necessary to select a low-cost and highly stable substrate material, which should have abundant metal and good electrical conductivity, as well as a large specific surface area and multiple active centers. Among the many 2D materials, materials with metallic properties are a good choice. However, due to the wide variety of 2D materials, sifting through thousands of candidates remains a major challenge. The process of screening hydrogen evolution electrocatalysts can be greatly accelerated by using descriptors based on catalytic performance and density functional theory (DFT) calculations.<sup>41–43</sup> To address the current challenges in the screening of 2D materials as SAC substrate materials, we designed a study to focus on the possibility of anchoring transition metal atoms in novel 2D substrate materials, and here we explore and report on the importance of such SAC descriptors. Recently, through first-principles swarm intelligence structure calculations, several 2D B<sub>X</sub>N materials ( $X = 2, 3, 5$ ) have been successfully discovered. These B<sub>X</sub>N materials have high cohesion energy and good kinetic, thermodynamic and mechanical stability, making them highly feasible for experimental synthesis.<sup>44</sup> B<sub>X</sub>N materials also exhibit excellent recyclability and improved metal conductivity after TM loading, showing great potential for hydrogen evolution SAC applications.

In this work, based on first principles, we studied the catalytic activity in HER of TM single atoms loaded on B<sub>X</sub>N materials' surface, and discuss the mechanism of the high catalytic activity of the SCAs. Zhou *et al.* have verified the structural stability of 2D B<sub>X</sub>N materials through phonon spectrum calculation and *ab initio* molecular dynamics simulation (AIMD).<sup>44</sup> We studied a variety of transition metal elements, including the 3d, 4d, and 5d groups. Here, the catalytic activity of SACs in HER is described by the Gibbs free energy change ( $G_{H^+}$ ) of hydrogen adsorption. The descriptors proposed in this paper only include some inherent properties of substrate materials and provide a simple and rapid method for designing and screening HER electrocatalysts more effectively. Additionally, the optimal HER activity of 2D B<sub>X</sub>N catalysts in all pH ranges was investigated. Ti-, V-, Y- and Zr-embedded B<sub>5</sub>N SACs have high HER activity with moderate and good electrical conductivity before and after H binding at pH = 0. In addition, the 3d-B<sub>2</sub>N, 3d-B<sub>3</sub>N, 3d-B<sub>5</sub>N and 4d-B<sub>5</sub>N SACs studied have high activity over a wide pH range. Specifically, 3d-B<sub>2</sub>N and 3d-B<sub>3</sub>N SACs are suitable for acidic environments, and 4d-B<sub>5</sub>N SACs are suitable for alkaline environments, because the electron state near the Fermi level increases and the charge density on the surface increases. The high concentration of free charges is a key factor in HER progression.

## 2. Computational methods

All spin-polarized calculations in this section were performed by using the vienna *ab initio* simulation package (VASP)<sup>45,46</sup> based on density functional theory. The generalized gradient approximation (GGA)<sup>47</sup> of the Perdew–Burke–Ernzerhof (PBE)<sup>48</sup> functional was used to describe the exchange correlation energy, and the projection plane-wave (PAW) method<sup>49</sup> was used to describe the pseudopotential of all atoms. In order to eliminate the influence of van der Waals (vdW) forces, Grimme's empirical correction method, namely, DFT+D3,<sup>50,51</sup> was used in structural optimizations and property calculations of the 2D B<sub>X</sub>N materials. A cutoff energy of 500 eV for the plane-wave basis was adopted. The energy and force convergence criteria for self-consistent optimizations were set to  $10^{-5}$  eV and  $10^{-3}$  eV Å<sup>-1</sup>, respectively. In the process of structural optimization, the inverted vector  $k$ -point grids of 2D B<sub>X</sub>N materials were divided into  $2\pi \times 0.03$  Å<sup>-1</sup>. It is worth mentioning that when calculating electronic properties, the inverted lattice vector  $k$ -point grid for all structures in the self-consistent iteration process was set to a larger value. A  $2 \times 2 \times 1$  monolayer of 2D B<sub>X</sub>N materials was adapted for all calculations, and a vacuum space of 20 Å along the  $z$  direction was included to prevent interactions between periodic images. In *ab initio* molecular dynamics (AIMD) simulations, integration of the equations of motion proceeded with time steps of 1.0 fs for different temperature ranges.<sup>52</sup> Typical simulations ran for 3000 steps with the time scale of about 3 ps. The isokinetic ensemble (NVT) was employed for the ions, where the ion temperature  $T_i$  was fixed using velocity scaling. As is well known, the influence of the solvation effect on the process of hydrogen adsorption is so slight that the solvation effect can be omitted, so we will not consider the calculations of solvation effect in this work.<sup>52–55</sup> For more computational details, please see the ESI.†

## 3. Results and discussion

According to previous reports, the B<sub>2</sub>N, B<sub>3</sub>N and B<sub>5</sub>N structures were constructed in diverse orthorhombic configuration with the space group of AMM2, AMM2 and PMC21, respectively.<sup>44</sup> Fig. 1(a)–(c) illustrate the schematic diagrams of the 2D B<sub>X</sub>N materials ( $X = 2, 3, 5$ ), which are composed of three different unit cells, respectively. The common feature is the presence of a five-member ring or even a six-member ring formed by boron atoms crossing with the nitrogen atoms in all the 2D B<sub>X</sub>N materials' unit cells. The optimized lattice constant of 2D B<sub>X</sub>N materials is calculated to be  $a = 10.29$  Å,  $b = 3.91$  Å ( $X = 2$ );  $a = 10.13$  Å,  $b = 4.80$  Å ( $X = 3$ ); and  $a = 6.41$  Å,  $b = 2.69$  Å ( $X = 5$ ), respectively, in good accordance with previous studies.<sup>44</sup> In order to explore the TM adsorption behavior on the surface of 2D B<sub>X</sub>N materials, a  $2 \times 2$  supercell containing 72 atoms,  $2 \times 2$  supercell including 64 atoms and  $2 \times 2$  supercell involving 48 atoms as the substrate for the adsorption were constructed, correspondingly. Dynamic stability is an inevitable index in material design. So, in order to evaluate the dynamic stability of the B<sub>X</sub>N materials, we calculated their phonon



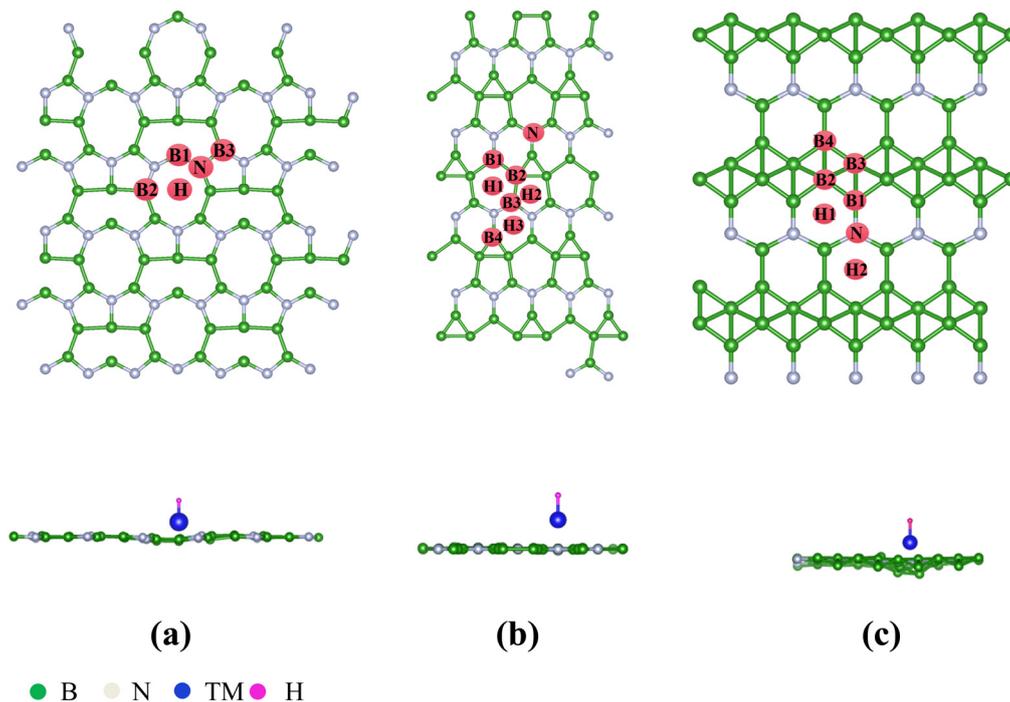


Fig. 1 Top and side views of the optimized structures of the 2D  $B_xN$  materials: (a)  $B_2N$  monolayer, (b)  $B_3N$  monolayer, and (c)  $B_5N$  monolayer with the TM and H being adsorbed at the optimal HER sites.

spectra. As shown in Fig. S1 (ESI<sup>†</sup>), no negative frequency is observed in the entire Brillouin region, indicating that the  $B_2N$ ,  $B_3N$  and  $B_5N$  monolayers have good dynamic stability. Three different sites are considered for TM adsorption on the  $B_xN$  materials, including the hollow of the surface B–N ring, the top site of B atom and the top site of surface N atom. Then, binding energy ( $E_b$ ) calculations were implemented to evaluate the stability and feasibility of experimental synthesis of SACs for each configuration based on eqn (S1) (ESI<sup>†</sup>). Isolated Sc, as the test atom, adsorbs on nine different configurations, and the  $E_b$  was calculated between the Sc atom and substrates. Finally, it can be found from Table S1 (ESI<sup>†</sup>) that among the adsorption configurations, Sc adsorption on the hollow of 2D  $B_xN$  material ( $X = 2, 3, 5$ ) surface is the most energetically favorable, with the  $E_b$  of  $-4.75$  eV,  $-3.91$  eV and  $-5.18$  eV, respectively. Then, the use of 2D  $B_xN$  materials as substrates to anchor single atoms of 3d, 4d, and 5d TM was further investigated, and the  $E_b$  between TM atom and  $B_xN$  materials was calculated. The corresponding  $E_b$ , cohesive energies ( $E_{coh}$ ) and the energy difference ( $\Delta E$ ) between  $E_b$  and  $E_{coh}$  of all  $TM@B_xN$  materials studied in the present work are shown in Fig. 2 and Fig. S2, S3 (ESI<sup>†</sup>). The  $E_{coh}$  can be calculated by the following equation:

$$E_{coh} = (E_{M(bulk)})/n \quad (1)$$

where  $E_{M(bulk)}$  is the energy of M crystals and  $n$  is the number of M atoms in the unit cell of crystals, and these values were compared with the adsorption energies. Because the energy advantage of TM clusters is essentially lower than that of metal crystals, to avoid the formation of clusters among TM atoms, we set a standard for judging system stability, that is,

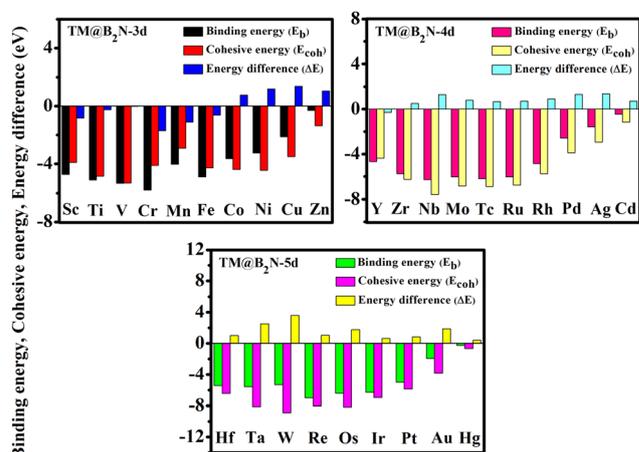


Fig. 2 Adsorption of different TM atoms on the  $B_2N$  monolayer and the corresponding binding energy ( $E_b$ ), cohesive energy ( $E_{coh}$ ) and their energy difference ( $\Delta E$ ).

$\Delta E < 0$  eV. As indicated in Fig. 2, the  $\Delta E$  values are positive for all 5d-TM@ $B_2N$  systems, and only six TM atoms of 3d state (Fe, Mn, Ti, V, Cr and Sc) and one TM atom of 4d state (Y) can immobilize on the  $B_2N$  materials with  $\Delta E < 0$  eV. Similarly, the calculated  $\Delta E$  values are positive for all 5d-TM@ $B_3N$  systems, and only Co, Fe, Cr, Mn and Mo atoms can adsorb stably on  $B_3N$  materials. For the  $B_5N$  system, it is obvious that the adsorption of TM atoms by  $B_5N$  materials is stronger than that by  $B_2N$  and  $B_3N$  materials. Most TM atoms, such as Co, Fe, Mn, Ti, V, Cr, Sc, Y, Zr, Nb, Mo, Tc, Ru and Ir, including the 3d, 4d and 5d groups, are effectively adsorbed on the  $B_5N$  materials.



For example, the  $E_b$  values of Mn@B<sub>5</sub>N and Cr@B<sub>5</sub>N SACs are even as low as  $-6.37$  eV and  $-6.55$  eV, respectively. The reason why the three 2D B<sub>x</sub>N materials have different adsorption effects on TM atoms is that they have different defect configurations. It is well known that for most 2D materials, the existence of surface atom vacancy is unavoidable to some extent. The main reason is that defect-induced structure disorder always leads to an entropy increase, which is thus in favour of balancing the defects caused a decrease of thermodynamic stability of the material.<sup>56–58</sup> This indicates that among 2D materials composed of the same chemical constituents with different configurations, a compound with larger defect concentration always has higher energy and thus shows lower thermodynamic stability than that with lower defect concentration.<sup>59–61</sup> This is because the larger structure of the defect configuration has more non-metallic atoms that combine with TM to form strong chemical bonds. Hence, for 2D B<sub>x</sub>N materials, B<sub>5</sub>N materials with relatively low defect concentration can accommodate more surface TM atoms, while B<sub>2</sub>N and B<sub>3</sub>N materials with relatively small defects have poor ability to adsorb surface TM atoms. The thermal stability of TM@B<sub>x</sub>N monolayers is simulated by AIMD. Fig. S4 (ESI†) shows that the mean value of the total potential energy during the AIMD simulation oscillates within a narrow range, and the overall configuration of Ti@B<sub>2</sub>N, Mn@B<sub>3</sub>N, Fe@B<sub>5</sub>N and Mo@B<sub>5</sub>N monolayers remains good after 3 ps AIMD simulation, which confirms their thermal stability.

To study the electronic characteristics of the TM@B<sub>x</sub>N systems, the density of states (DOS) spectra of all pre-screened SACs are given in Fig. 3 and Fig. S5 (ESI†). It is obvious that there are more pronounced electronic states near the Fermi level ( $E_F$ ) of the orbital resolved DOS spectra of TM@B<sub>x</sub>N materials compared with the DOS spectra of pure 2D B<sub>x</sub>N materials. This is because the symmetry of 2D B<sub>x</sub>N materials is broken after the addition of TM atoms, thereby generating more unsaturated electrons. Thus, it can be seen that TM atoms are the major contributors of electron densities near  $E_F$ , which is offered principally by the d orbitals of TM atoms, rendering the 2D B<sub>x</sub>N materials metallic. This is conducive to the improvement of surface electrical conductivity of SACs, thus enhancing their catalytic activity.

In order to more intuitively demonstrate the metallic nature of SACs, the electronic conductivity of TM@B<sub>x</sub>N systems was further calculated. According to Fig. S6 (ESI†), it can be clearly found that the studied SACs have good surface conductivity, which is conducive to improving the catalytic activity of SACs. Hence, the HER activity of the pre-screened TM@B<sub>x</sub>N SACs is achieved by setting TM atoms as the active sites. These stable TM@B<sub>x</sub>N systems as HER catalysts were next investigated. It is well known that the  $\Delta G_{H^*}$  of atomic hydrogen adsorption is a key descriptor for evaluating HER catalytic activity.<sup>62</sup> Thus, we systematically studied the TM@B<sub>x</sub>N systems in accordance with the calculation of  $\Delta G_{H^*}$  in acidic and alkaline conditions, respectively. In the acid conditions, the HER process can be

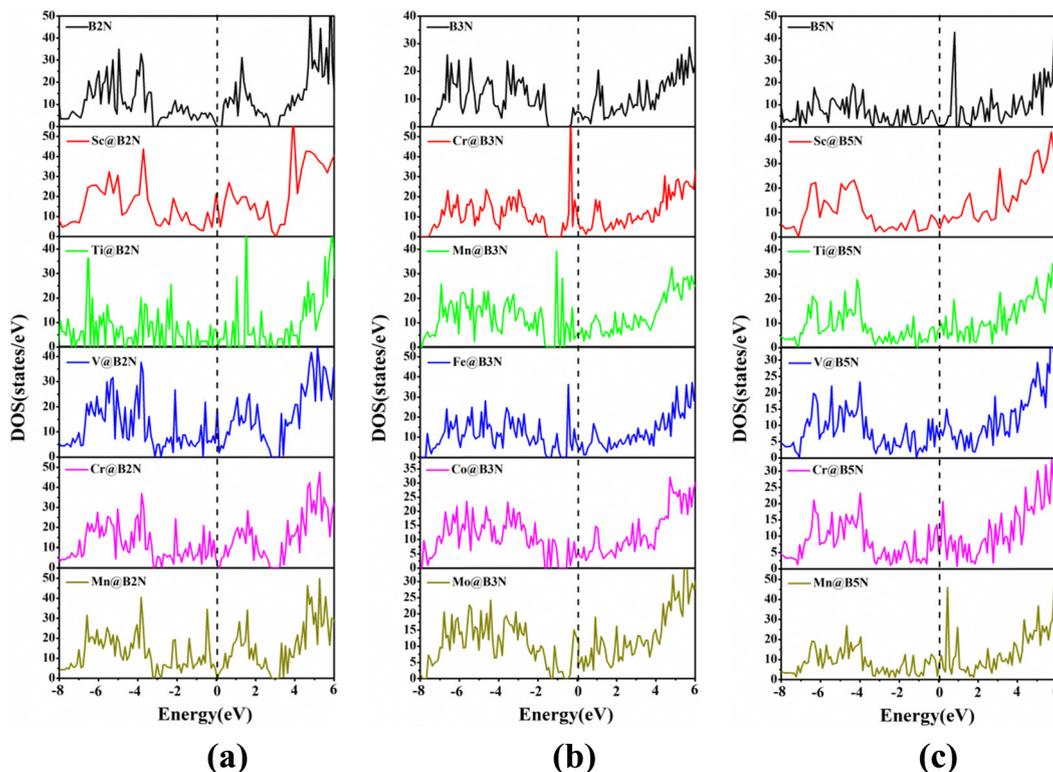
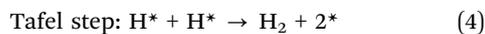
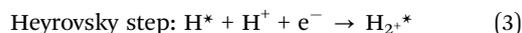
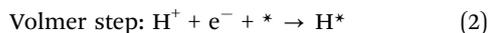


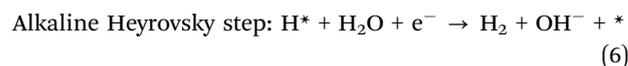
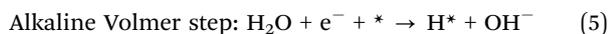
Fig. 3 The density of states (DOS) spectra for (a) TM@B<sub>2</sub>N, (b) TM@B<sub>3</sub>N and (c) TM@B<sub>5</sub>N. The Fermi levels are set to zero and indicated by black dashed lines.



expressed by Volmer–Tafel and Volmer–Heyrovsky reaction pathways. The two reaction equations are divided into three key steps:



where \* and H\* represent the active site on the catalyst surface and the intermediate hydrogen adsorbed on the surface, respectively. For the Heyrovsky reaction, H<sub>2</sub> is generated when adsorbed hydrogen (H\*) interacts with H<sub>3</sub>O<sup>+</sup> clusters. As shown in Fig. S7 (ESI<sup>†</sup>), the calculated energy barrier for the Heyrovsky pathway of the Ti@B<sub>5</sub>N monolayer is 1.78 eV, while the activation energy barrier of the Tafel reaction of the Ti@B<sub>5</sub>N monolayer is 0.52 eV. Thus, the HER mechanism of the Ti@B<sub>5</sub>N monolayer may follow the Tafel-dominated Volmer–Tafel reaction. Similarly, the HER mechanism of the V@B<sub>5</sub>N monolayer also follows the Volmer–Tafel reaction. Nevertheless, under alkaline conditions, water dissociation produces hydrogen ions (H<sup>+</sup>), and the two important reaction steps are given as follows:



Under alkaline conditions, the apparent HER activity is limited by hydrolytic dissociation, which produces H\* and is sensitive to pH, so the energy barrier of hydrolytic dissociation needs to be considered. At the same time, more and more computational and experimental studies have proven that the hydrolytic separation energy barrier plays an important role in the alkaline hydrogen evolution process. As shown in Fig. S8 (ESI<sup>†</sup>), it is found through calculation that Ti- and V-modified B<sub>5</sub>N have rapid hydrolysis dissociation ability, with the energy barrier of about 0.23 and 0.09 eV, which can realize rapid proton transfer. Therefore, Ti, V and BS-B1P1 can cooperate well to accelerate alkaline HER.

Fig. 4 shows the  $\Delta G_{\text{H}^*}$  for single H atom adsorption on TM@B<sub>x</sub>N systems at pH = 0. Ti@B<sub>5</sub>N, V@B<sub>5</sub>N, Y@B<sub>5</sub>N and Zr@B<sub>5</sub>N SACs show excellent catalytic activity with  $\Delta G_{\text{H}^*}$  values of −0.027, −0.094, 0.073 and −0.04 eV, respectively. It can be seen that the  $\Delta G_{\text{H}^*}$  of these SACs are even low as  $\sim -0.027$  eV, superior to precious metals such as Pt. In reality, electrocatalysts need to undergo charge adjustment to match their Fermi level with the applied electrode potential, and therefore, a grand-canonical ensemble of electrons under the constant

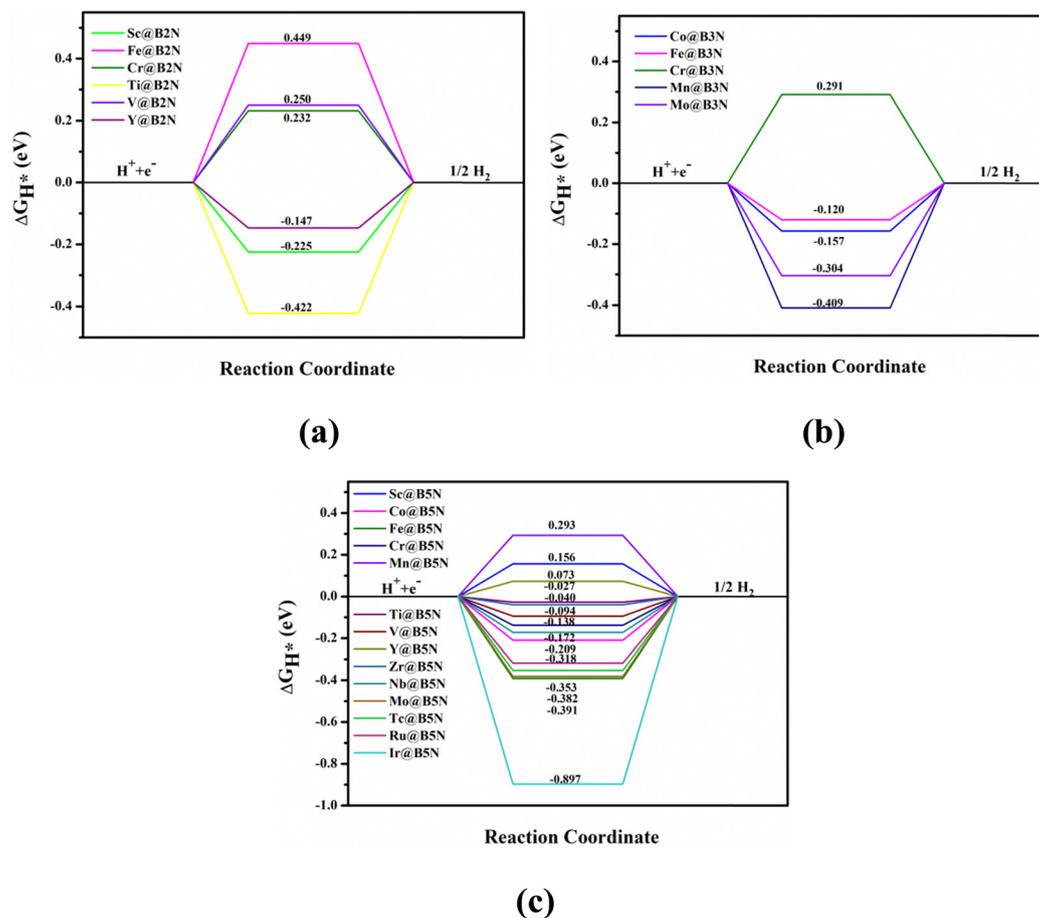


Fig. 4 Free energy diagram for HER of different TM atoms on the (a) B<sub>2</sub>N, (b) B<sub>3</sub>N, and (c) B<sub>5</sub>N monolayer compounds under standard conditions.



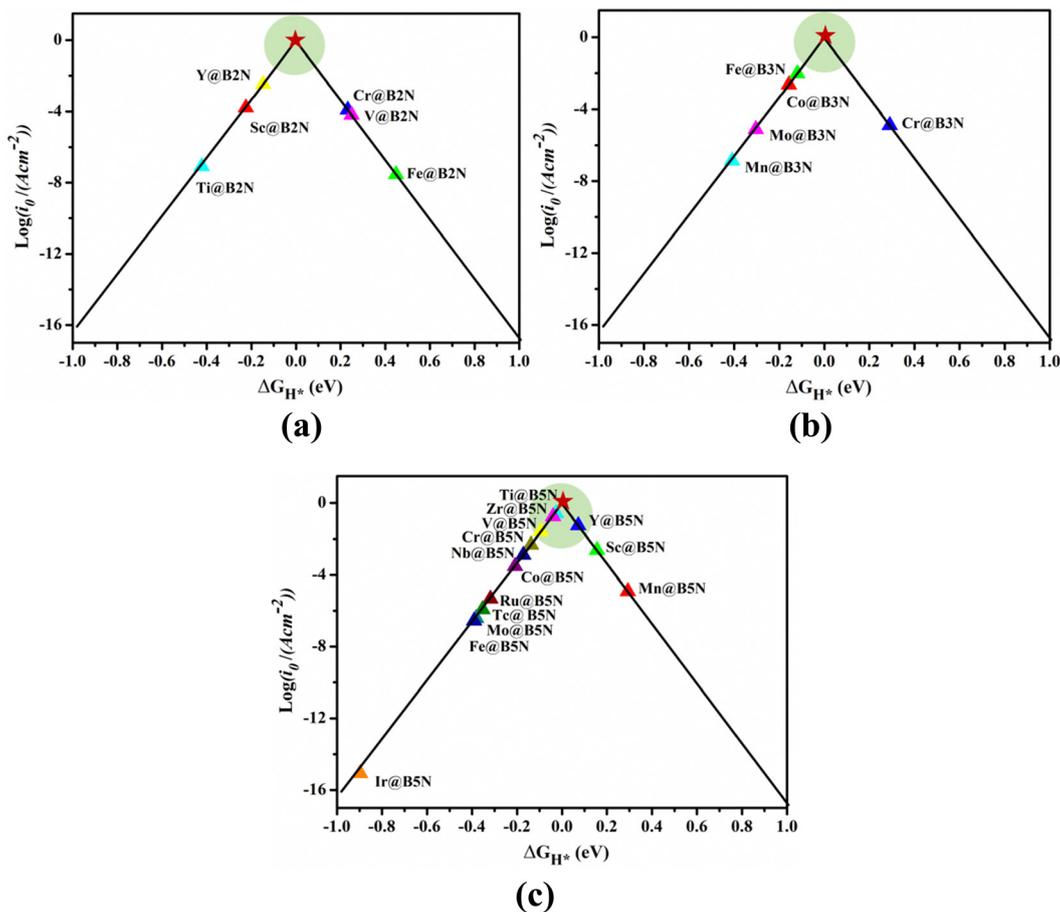


Fig. 5 HER volcano curve of exchange current ( $i_0$ ) as a function of the Gibbs free energy change ( $\Delta G_{H^*}$ ) of hydrogen adsorption on (a) TM@B<sub>2</sub>N, (b) TM@B<sub>3</sub>N, and (c) TM@B<sub>5</sub>N systems.

potential model (CPM) is better at reflecting practical electrocatalytic conditions.<sup>63,64</sup> We supplemented the calculation of  $\Delta G_{H^*}$  corresponding to different potentials under the CPM model. According to Fig. S9 (ESI<sup>†</sup>), it can be clearly found that TM@B<sub>5</sub>N SACs with good catalytic performance show little change in  $\Delta G_{H^*}$  at different potentials, and still have excellent catalytic performance. In addition, TM@B<sub>5</sub>N SACs have the best HER catalytic active sites on the hollow of the 2D B<sub>5</sub>N surface. Nevertheless, the decoration of TM atoms can reinforce well the binding of H atoms to the B<sub>2</sub>N and B<sub>3</sub>N materials, but it performs poorly in enhancing the HER catalytic activity of the TM@B<sub>2</sub>N and TM@B<sub>3</sub>N SACs, showing inferior  $\Delta G_{H^*}$  values. This means that at pH = 0, low-cost TM@B<sub>5</sub>N SACs may become substitutes for precious metal catalysts to improve the performance of HER. To more intuitively compare the catalytic activity of TM@B<sub>x</sub>N SACs at pH = 0, the corresponding volcano curves are plotted in Fig. 5. According to Norskov's hypothesis, where a simple kinetic model is established to understand the origin of the volcano, the exchange current density ( $i_0$ ) based on  $\Delta G_{H^*}$  was studied and calculated.<sup>65</sup> When  $\Delta G_{H^*} < 0$ , the expression of exchange current is expressed as:

$$i_0 = -ek_0 \frac{1}{1 + \exp(-\Delta G_{H^*}/k_B T)} \quad (7)$$

when  $\Delta G_{H^*} > 0$ , the exchange current is:

$$i_0 = -ek_0 \frac{1}{1 + \exp(\Delta G_{H^*}/k_B T)} \quad (8)$$

where  $k_0$  is the rate constant and  $k_B$  is the Boltzmann constant. Because there are no experimental data available,  $k_0$  is set to 1.<sup>66</sup> First, the volcano map is drawn with  $\Delta G_{H^*}$  as the horizontal coordinate and  $i_0$  as the vertical coordinate. The HER catalytic activity of these SACs can be better observed based on the position of  $\Delta G_{H^*}$  and  $i_0$  relative to the volcanic peak, where the closer the location is to the volcanic peak, the higher the HER activity of the SACs. As shown in Fig. 5(c), Ti@B<sub>5</sub>N, V@B<sub>5</sub>N, Y@B<sub>5</sub>N and Zr@B<sub>5</sub>N systems achieve the maximum exchange current rates on account of the appropriate interactions between TM (Ti, V, Y, Zr) and H atoms, implying a promising catalytic activity for HER. However, most TM@B<sub>2</sub>N SACs, such as Co@B<sub>2</sub>N, Cr@B<sub>2</sub>N, Fe@B<sub>2</sub>N, Nb@B<sub>2</sub>N, Ru@B<sub>2</sub>N, Tc@B<sub>2</sub>N, Mo@B<sub>2</sub>N and Ir@B<sub>2</sub>N, exhibit poor HER performance due to the strong bonding strength between H atoms and TM atoms, and are mainly distributed on the left side of the volcano map. Sc@B<sub>2</sub>N and Mn@B<sub>2</sub>N SACs are on the right side of the volcano map because of the weak interaction between H and TM atoms, which results in positive  $\Delta G_{H^*}$  values. However, among the



pre-screened TM@B<sub>2</sub>N (TM = Sc, Cr, V, Ti, Fe and Y) and TM@B<sub>3</sub>N (TM = Co, Cr, Fe, Mn and Mo) SACs (shown in Fig. 5(a) and (b)), Ti-, Mn-, and Y@B<sub>2</sub>N; and Co-, Fe-, Mn-, Mo@B<sub>3</sub>N are mainly distributed on the left side of the volcano diagram, showing strong hydrogen adsorption, to the disadvantage of the release of atomic hydrogen. V-, Fe-, Cr@B<sub>2</sub>N and Cr@B<sub>3</sub>N SACs are on the right side of the volcano curve with highly positive  $\Delta G_{\text{H}^*}$  values, which is not conducive to the adsorption of atomic hydrogen on the TM atom, thus exhibiting low  $i_0$  values. It is obvious that most SACs have negative  $\Delta G_{\text{H}^*}$  values because of the strong adsorption between hydrogen atoms and TM atoms. However, pH modification can effectively improve the catalytic activity of these SACs, so as to have a suitable  $\Delta G_{\text{H}^*}$  value. In neutral or alkaline environment, water molecules (H<sub>2</sub>O) are first adsorbed and decomposed on the SAC surface (Volmer process: H<sub>2</sub>O + e<sup>-</sup> + \* → H\* + OH<sup>-</sup>). Then, two adjacent adsorbed hydrogen atoms on the SAC surface will combine to form a molecule of hydrogen (Heyrovsky process: H\* + H<sub>2</sub>O + e<sup>-</sup> → H<sub>2</sub> + OH<sup>-</sup> + \*). SACs in this process promote the formation of hydrogen molecules.

We can regard the effect of pH on  $\Delta G_{\text{H}^*}$  as an additional entropic potential. Then the pH-dependent  $\Delta G(\text{pH})$  can be obtained by eqn (S7) (ESI<sup>†</sup>):  $\Delta G(\text{pH}) = k_{\text{B}}T \ln(10) \times \text{pH}$ , which is conducive to understanding the relationship between HER performance and pH. Fig. 6(a)–(d) show the effect of different

pH on the HER performance of all pre-screened SACs, including 3d-, 4d and 5d-TM@B<sub>x</sub>N systems. It is obvious that as the pH value is increased from 1 to 14,  $\Delta G_{\text{H}^*}$  value gradually increases, meaning that the adsorption inclination between hydrogen atom and SACs significantly decreases. By exploring the dependence of H adsorption on different SACs with pH, the optimal SACs for HER can be found. Fig. 6(c and d) show the linear relationship between the pH and  $\Delta G_{\text{H}^*}$  of TM@B<sub>5</sub>N SACs. Fig. 6(c) indicates that for 3d-TM@B<sub>5</sub>N SACs, only V@B<sub>5</sub>N and Ti@B<sub>5</sub>N systems lie in the optimal HER activity range at pH = 0. With increasing pH from 0 to 3, HER activity of the V@B<sub>5</sub>N and Ti@B<sub>5</sub>N SACs decreases,  $\Delta G_{\text{H}^*}$  increases from -0.027 to 0.100 eV, indicating that V@B<sub>5</sub>N and Ti@B<sub>5</sub>N SACs can maintain ultra-high HER activity in a strong acid environment. Cr@B<sub>5</sub>N and Co@B<sub>5</sub>N SACs can only have excellent catalytic activity in strong acid or weak acid environment, with pH regulation from 2 to 6. It is worth mentioning that Fe@B<sub>5</sub>N SAC can effectively catalyze HER under weak acid, neutral and alkaline conditions, which means that Fe@B<sub>5</sub>N SAC has a wide range of choices in different pH environments. Fig. 6(d) gives the  $\Delta G_{\text{H}^*}$  vs. pH for the 4d and 5d-TM@B<sub>5</sub>N SACs. Compared with 3d-TM@B<sub>5</sub>N SACs, the effect of pH on 4d and 5d-TM@B<sub>5</sub>N SACs is more obvious, which is reflected in their obvious increase of catalyst activity in the pH range from 0 to 14. As can be seen from the figure at pH = 0, the adsorption between 4d,

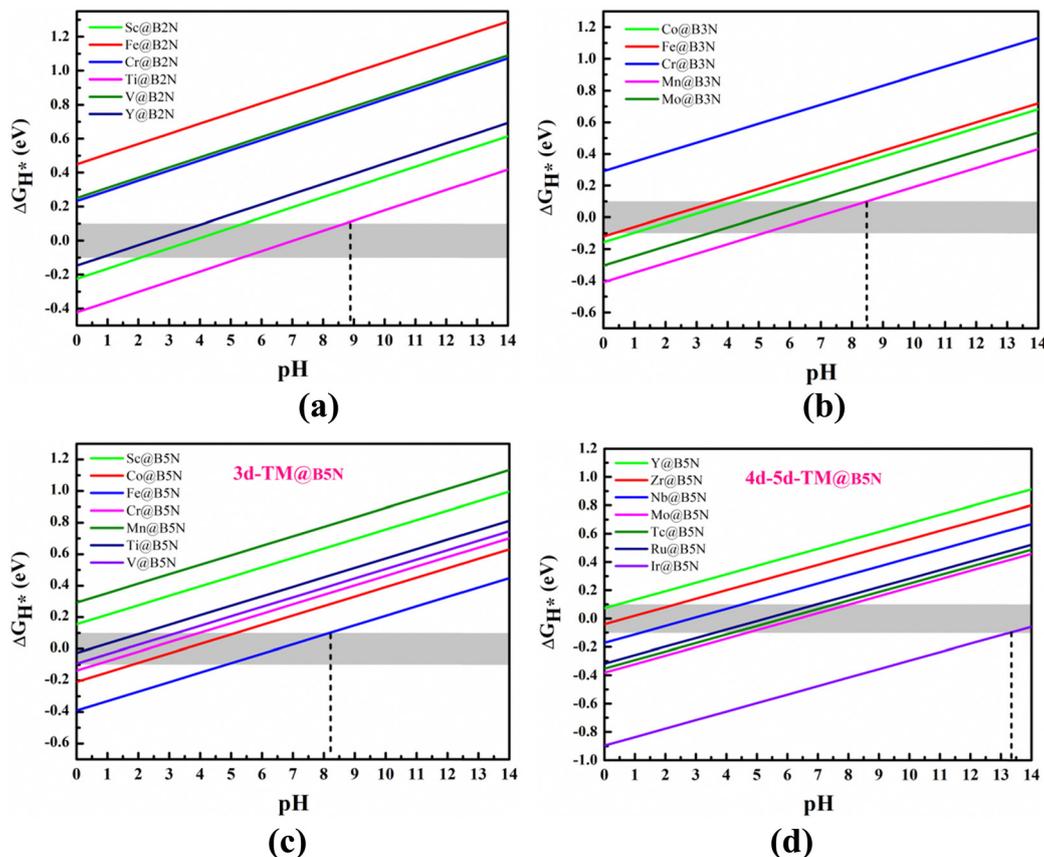


Fig. 6 The pH dependence of H-adsorption free energy of TM atom adsorption on the (a) B<sub>2</sub>N, (b) B<sub>3</sub>N and (c) and (d) B<sub>5</sub>N monolayer compounds. The pink shaded area in the figures indicates the ideal  $\Delta G_{\text{H}^*}$  value range.



5d TM atoms and H atom is too strong, leading to a more negative  $\Delta G_{H^*}$ . As pH increases, the bonding strength between 4d, 5d TM atoms and the H atom is further weakened, bringing  $\Delta G_{H^*}$  down to a suitable value. In the pH range of 0 to 2.5, that is, under strong acid conditions, Y@B<sub>5</sub>N and Zr@B<sub>5</sub>N SACs are highly active in HER. In contrast, Ir@B<sub>5</sub>N SAC has good catalytic activity in a strong alkali environment. Nb@B<sub>5</sub>N SAC can maintain excellent HER activity under a stronger acid environment with pH range of 2 to 4.5, while only under the condition of weak acid with pH range of 4 to 7 can Ru@B<sub>5</sub>N and Tc@B<sub>5</sub>N SACs effectively catalyze HER. Similar to Fe@B<sub>5</sub>N SAC, Mo@B<sub>5</sub>N SAC can also play a catalytic role under weak acid, neutral and alkaline conditions. The variation of  $\Delta G_{H^*}$  with pH of TM@B<sub>2</sub>N SACs is shown in Fig. 6(a). It is obvious that TM@B<sub>2</sub>N SACs mainly promote HER under acidic conditions. For example, Sc@B<sub>2</sub>N and Y@B<sub>2</sub>N SACs are active under the weak-acid or strong-acid condition with pH range of 1 to 5.5, and the HER performance of Ti@B<sub>2</sub>N SAC can be greatly improved in either acidic, neutral or alkaline conditions with pH range of 5.5 to 9. As seen in Fig. 6(b), TM@B<sub>3</sub>N SACs also catalyze the conversion process from atomic H to H<sub>2</sub> mainly under acidic conditions. Fe@B<sub>3</sub>N and Co@B<sub>3</sub>N SACs have excellent catalytic activity in strong acid environment with pH regulation from 1 to 4. Mo@B<sub>3</sub>N SAC shows stronger HER catalysis in the weak acid environment, with the pH range of 4 to 7. Interestingly, Mn@B<sub>3</sub>N SAC can be effectively adjusted by pH and gives weak acid, neutral and alkaline HER activity within the pH range of 5 to 8.5. In short, our results suggest that the HER activity of TM@B<sub>x</sub>N SACs is closely associated with pH. The TM@B<sub>x</sub>N SACs are not only catalytically active in acidic conditions but also exhibit high HER catalytic activity in alkaline environments. Remarkably, Ti@B<sub>2</sub>N, Mn@B<sub>3</sub>N, Fe@B<sub>5</sub>N and Mo@B<sub>5</sub>N SACs have potential to be a multifunctional catalyst with a wide pH threshold.

## 4. Conclusions

In summary, we designed promising SACs composed of 3d-, 4d-, and 5d-TM atoms and 2D B<sub>x</sub>N materials toward efficient HER using first-principles calculations. Some stable TM@B<sub>x</sub>N SACs were screened by theoretical calculations, and DOS calculations show that these SACs have good electrical conductivity, providing favorable conditions for rapid transfer among electrons. In addition, free energy calculations showed that the TM@B<sub>x</sub>N SACs exhibit different catalytic performance in different pH ranges. Ti-, V-, Y- and Zr-embedded B<sub>5</sub>N SACs have high HER activity with moderate and good electrical conductivity before and after H binding at pH = 0. TM@B<sub>2</sub>N and TM@B<sub>3</sub>N SACs have excellent HER performance in acid environment. Remarkably, three different TM@B<sub>x</sub>N systems have appropriate SACs which can maintain high HER catalytic activity in acidic, neutral and alkaline environments to promote the conversion of atomic H to H<sub>2</sub>. Therefore, our works demonstrate that the cost-effective TM@B<sub>x</sub>N can serve as SACs to facilitate HER, which provides a theoretical reference for future application in practice.

## Data availability

All data generated or analyzed during this study are included in this published article and its ESI† files.

## Conflicts of interest

The authors report no conflicts of interest. The authors alone are responsible for the content and writing of the paper.

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