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433

## Mo<sub>2</sub>B<sub>2</sub> MBene-supported single-atom catalysts as bifunctional HER/OER and OER/ORR electrocatalysts†

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Searching for highly efficient and cost-effective bifunctional electrocatalysts for the oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), which can be applied to water splitting, fuel cells and metal–air batteries, is critical for developing clean and renewable energies. Yet it remains a great challenge. By means of first-principles calculations, we have studied the OER, ORR and HER catalytic activity of Mo<sub>2</sub>B<sub>2</sub> MBene-supported single-atom catalysts (SACs) by embedding a series of transition metal atoms in the Mo vacancy (TM@Mo<sub>2</sub>B<sub>2</sub>, TM = Ti, V, Cr, Mn, Fe, Co, Ni and Cu) as electrocatalysts. All TM@Mo<sub>2</sub>B<sub>2</sub> SACs show excellent metallic conductivity, which would be favorable for the charge transfer in electrocatalytic reactions. Importantly, Ni@Mo<sub>2</sub>B<sub>2</sub> can be used as a HER/OER bifunctional electrocatalyst with a lower  $|\Delta G_H|$  (−0.09 eV) for the HER under 1/4H coverage and a lower overpotential ( $\eta_{OER} = 0.52$  V) than that of IrO<sub>2</sub> ( $\eta_{OER} = 0.56$  V) for the OER, while Cu@Mo<sub>2</sub>B<sub>2</sub> can be used as an OER/ORR bifunctional electrocatalyst with a lower overpotential ( $\eta_{OER} = 0.31$  V) than that of IrO<sub>2</sub> ( $\eta_{OER} = 0.56$  V) and RuO<sub>2</sub> ( $\eta_{OER} = 0.42$  V) for the OER and a lower overpotential of 0.34 V than that of Pt ( $\eta_{ORR} = 0.45$  V) for the ORR, for both of which the transition metal atoms serve as the active sites. This work could open up an avenue for the development of non-noble-metal-based bifunctional MBene electrocatalysts.

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### 1. Introduction

Clean and renewable energy technologies, such as water splitting, fuel cells and metal–air batteries, are crucial to mitigate environmental pollution and the energy crisis.<sup>1–10</sup> The bases of these technologies are the oxygen evolution reaction (OER), oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER), the efficiency of which mainly depends on the performance of the catalysts. Currently, the most effective catalysts are Pt (for the ORR and HER) and IrO<sub>2</sub>/RuO<sub>2</sub> (for the OER).<sup>11–14</sup> However, the scarcity and high price prevent their large-scale usage. Although great effort has been made in the research on OER, ORR and HER catalysts, such as nanostructured metal carbides,<sup>15–17</sup> graphene doped with heteroatoms,<sup>18,19</sup> carbon-based hybrids,<sup>20–22</sup> and transition metal chalcogenides,<sup>23,24</sup> searching for non-noble metal catalysts with high catalytic performance comparable to that of the above-mentioned Pt and IrO<sub>2</sub>/RuO<sub>2</sub> is still a great challenge. In addition, compared with two separate

unifunctional catalysts, for which the optimal working conditions are not always the same, bifunctional catalysts operating under optimal and identical conditions have many obvious advantages,<sup>25</sup> such as reducing costs and simplifying the systems.<sup>5</sup> According to previous work,<sup>3,26,27</sup> HER/OER bifunctional catalysts and OER/ORR bifunctional catalysts have attracted widespread attention because HER/OER bifunctional catalysts can be used for water splitting and OER/ORR bifunctional catalysts be used in fuel cells and metal–air batteries.

On account of the special physical and chemical properties and the large specific area, two-dimensional (2D) materials have been highly attractive in the past few years.<sup>28,29</sup> Recently, 2D transition metal borides, known as MBenes, have been extensively studied.<sup>30–35</sup> MBenes can be obtained by selectively removing the A atomic layer in MAB phases experimentally, where A represents aluminum in most cases, M represents a transition metal and B represents boron. So far, some MBenes including Mo<sub>2</sub>B<sub>2</sub>,<sup>33</sup> Cr<sub>2</sub>B<sub>2</sub> (ref. <sup>31</sup>) and Ti<sub>2</sub>B<sub>2</sub> (ref. <sup>35</sup>) have been experimentally produced. Importantly, according to previous work,<sup>30,32,35</sup> all the reported MBenes show good metallic conductivity to ensure electron transfer efficiency as electrodes and electrocatalysts. In addition, with the exploration and development of materials synthesis methods, the rational design of catalysts with high efficiency has become more intriguing. Among various catalyst designs, single-atom catalysts (SACs) have attracted significant attention, due to the

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unique electronic structure originating from the strong interaction and large charge transfer between the single metal atoms and the coordination species of the supports.<sup>36–38</sup> Moreover, SACs have fully exposed and dispersed active sites.<sup>39–42</sup> The unique electronic-structural properties and the exposure of the active sites make SACs exhibit remarkable enhancements in the catalytic performance in a variety of reactions.<sup>36</sup> Inspired by the good metallic conductivity and the large specific area of MBenes and the advantages of SACs, it is of significance to investigate MBene-supported SACs.

In this work, we rationally embedded transition metal atoms in the Mo vacancies of  $\text{Mo}_2\text{B}_2$  MBenes ( $\text{TM}@\text{Mo}_2\text{B}_2$ ) to construct SACs to study their OER, ORR and HER performance at different surface active sites by first-principles calculations, where the transition metals refer to Ti, V, Cr, Mn, Fe, Co, Ni and Cu. With good structural stability and metallic conductivity,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  can be used as bifunctional HER/OER and OER/ORR catalysts, respectively.

## 2. Computational methods

In this work, all the first-principles calculations were performed using spin-polarized density-functional theory (DFT) as implemented in the Vienna ab-initio simulation package (VASP) code.<sup>43</sup> The generalized gradient approximation (GGA) in the form of the Perdew–Burke–Ernzerhof (PBE) functional<sup>44</sup> was applied to describe the electron exchange–correlation interactions. To describe the long-range van der Waals interactions, the DFT+D2 method was used in this work.<sup>45</sup> The DFT+U correction was considered during the electronic structure calculations for the systems. The cut-off energy was set to 500 eV and  $4 \times 4$  supercells were used. The structural optimizations and electronic properties were all studied with the energy converged to  $1.0 \times 10^{-4}$  eV per atom and the force converged to 0.01 eV  $\text{\AA}^{-1}$ . In addition, the Brillouin zones were sampled with a  $4 \times 4 \times 1$   $k$ -point grid for structural optimizations, a  $7 \times 7 \times 1$   $k$ -point grid for static self-consistent calculations and a denser  $11 \times 11 \times 1$   $k$ -point grid for the density of states (DOS) calculations. To evaluate the stability of the catalysts, *ab initio* molecular dynamics (AIMD) simulations were performed. The AIMD simulations lasted for 10 ps with a time step of 2.0 fs at 300 K. The climbing-image nudged elastic band (NEB) method was used to investigate the diffusion pathway and energy barrier of intermediates for the OER and ORR, respectively.

The formation energy of Mo vacancies in  $\text{Mo}_2\text{B}_2$  is calculated using the following equation:

$$E_f(\text{V}_{\text{Mo}}) = E_{\text{Mo}_2\text{B}_2-\text{V}_{\text{Mo}}} - E_{\text{Mo}_2\text{B}_2} + n\mu_{\text{Mo}} \quad (1)$$

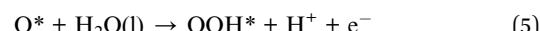
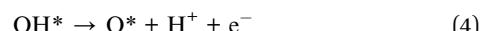
where  $E_{\text{Mo}_2\text{B}_2-\text{V}_{\text{Mo}}}$  and  $E_{\text{Mo}_2\text{B}_2}$  represent the total energy of the  $\text{Mo}_2\text{B}_2$  monolayer with and without Mo vacancies, respectively,  $\mu_{\text{Mo}}$  is the chemical potential of a Mo atom, and  $n$  stands for the number of Mo vacancies, which is 1 here to study the formation energy of a monovacancy.

The binding energy ( $E_b$ ) of transition metal atoms ( $\text{TM} = \text{Ti, V, Cr, Mn, Fe, Co, Ni and Cu}$ ) embedded in the Mo monovacancy of  $\text{Mo}_2\text{B}_2$  was calculated according to the equation:

$$E_b = E_{\text{TM}+\text{S}} - E_{\text{S}} - E_{\text{TM}} \quad (2)$$

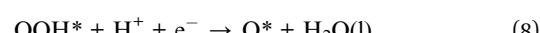
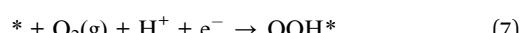
where  $E_{\text{TM}+\text{S}}$  and  $E_{\text{S}}$  represent the total energy of the defective  $\text{Mo}_2\text{B}_2$  with and without the embedded transition metal atoms, respectively, and  $E_{\text{TM}}$  represents the total energy of the transition metal atom from its most stable bulk phase.

The pathways of the OER, ORR and HER have been summarized in detail. In an acid electrolyte, the OER can be decomposed into the following elementary steps:



where \* represents the active site on the surfaces of the catalysts and l and g represent the liquid phase and the gas phase, respectively.

The ORR process can be regarded as the inverse of the OER process, which proceeds *via* the four-electron-transfer pathway as shown below:



For each elementary step of the OER and ORR, the free energies have been calculated according to the method proposed by Norskov *et al.*<sup>12</sup> The free energy change from the initial state to the final state of the reaction is defined as:

$$\Delta G = \Delta E + \Delta E_{\text{ZPE}} - T\Delta S + \Delta G_{\text{U}} + \Delta G_{\text{pH}} \quad (11)$$

where  $\Delta E$ ,  $\Delta E_{\text{ZPE}}$  and  $\Delta S$  are the differences in the total energy obtained from DFT calculations, zero-point energy and entropy between the reactants and the products, respectively.  $T$  represents temperature (298.15 K).  $\Delta G_{\text{U}} = -neU$ , where  $U$  is the applied electrode potential,  $e$  is the charge transferred and  $n$  is the number of proton–electron transferred pairs. In addition,  $\Delta G_{\text{pH}} = -k_{\text{B}}T\ln[\text{H}^+] = \text{pH} \times k_{\text{B}}T\ln 10$ , where  $k_{\text{B}}$  is the Boltzmann constant.

The free energy change for the four elementary OER steps can be obtained as:  $\Delta G_1 = \Delta G_{\text{OH}^*}$ ,  $\Delta G_2 = \Delta G_{\text{O}^*} - \Delta G_{\text{OH}^*}$ ,  $\Delta G_3 = \Delta G_{\text{OOH}^*} - \Delta G_{\text{O}^*}$  and  $\Delta G_4 = 4.92 - \Delta G_{\text{OOH}^*}$ . For the ORR steps:  $\Delta G_{\text{a}} = -\Delta G_4$ ,  $\Delta G_{\text{b}} = -\Delta G_3$ ,  $\Delta G_{\text{c}} = -\Delta G_2$  and  $\Delta G_{\text{d}} = -\Delta G_1$ . Therefore, the overpotential that evaluates the performance of the OER and ORR is applied according to the following equations:

$$\eta_{\text{OER}} = \max\{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}/e - 1.23 \quad (12)$$

$$\eta_{\text{ORR}} = \max\{\Delta G_{\text{a}}, \Delta G_{\text{b}}, \Delta G_{\text{c}}, \Delta G_{\text{d}}\}/e + 1.23 \quad (13)$$

where 1.23 represents the equilibrium potential.<sup>11</sup>

Under acidic conditions, the overall reaction scheme of the HER can be written as:



The HER catalytic activity is described using the computed Gibbs free energy change of (14), which was obtained by using the equation:

$$\Delta G_{\text{H}} = \Delta E_{\text{H}} + \Delta E_{\text{ZPE}} - T\Delta S \quad (16)$$

where  $\Delta E_{\text{H}}$  is the adsorption energy of hydrogen and  $\Delta E_{\text{ZPE}}$  and  $\Delta S$  are the differences in the zero-point energy and entropy between the adsorbed hydrogen and the gas phase hydrogen.

### 3. Results and discussion

#### 3.1 Stability and active sites

First of all, the structural stability of TM@Mo<sub>2</sub>B<sub>2</sub> was studied. The atomic structure of TM@Mo<sub>2</sub>B<sub>2</sub> is shown in Fig. 1a. We calculated the vacancy formation energy of the Mo monovacancy of Mo<sub>2</sub>B<sub>2</sub>,  $E_{\text{f}}(\text{V}_{\text{Mo}})$ , which is 0.98 eV. Generally, the smaller the value of the vacancy formation energy, the more possible the formation of the vacancy. Comparing the vacancy formation energy of MoS<sub>2</sub> (5.85 eV for the S monovacancy)<sup>46</sup> and graphene (7.69 eV for the C monovacancy),<sup>47</sup> it is evident that Mo<sub>2</sub>B<sub>2</sub> MBene shows greater possibility to form the Mo monovacancy with a relatively low vacancy formation energy. Besides, the vacancy formation energy of Mo<sub>2</sub>B<sub>2</sub> MBene is comparable to that of M<sub>2</sub>C-type MXenes ranging from 0.96 to 2.85 eV, which make it easy to form vacancies.<sup>48</sup> Then, the binding energy ( $E_{\text{b}}$ ) of the transition metal atoms in TM@Mo<sub>2</sub>B<sub>2</sub> was calculated, and the results are depicted in Fig. 1b and Table S1.<sup>†</sup> As is well-known, the negative  $E_{\text{b}}$  indicates the high stability of the recombinant systems. The binding energy of Ti@Mo<sub>2</sub>B<sub>2</sub>, V@Mo<sub>2</sub>B<sub>2</sub>, Cr@Mo<sub>2</sub>B<sub>2</sub>, Mn@Mo<sub>2</sub>B<sub>2</sub>, Fe@Mo<sub>2</sub>B<sub>2</sub>, Co@Mo<sub>2</sub>B<sub>2</sub>, Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub> is -6.99, -5.97, -5.38, -4.55, -5.02, -4.74, -6.12 and -5.73 eV, respectively, implying that all the studied materials possess excellent structural stability. In

addition, as shown in Fig. 1c, the charge accumulation between TM and B atoms indicates the formation of TM-B bonds, which is consistent with the above-mentioned negative binding energy. In addition, we performed AIMD simulations and the result is shown in Fig. S1,<sup>†</sup> indicating that Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub> are both thermally stable.

Next, the active sites for the OER, ORR, and HER need to be studied. In Mo<sub>2</sub>B<sub>2</sub> MBenes, embedding the transition metal atoms in the Mo vacancies causes changes in the chemical environment around the embedded transition metal atoms. As shown in Fig. 1a, seven possible active sites of TM@Mo<sub>2</sub>B<sub>2</sub> are marked. According to previous work,<sup>28,30</sup> the HER always occurs on the metal atoms instead of boron atoms of MBenes. Hence, the Mo atoms (including the Mo atoms on the surface and Mo atom on the bridge sites) and TM atoms are selected to be the possible active sites for the HER, including sites I, II, III, IV and VII. For the OER and ORR, apart from the above active sites, the B atoms on the bridge sites are also included. Therefore, we studied the OER, ORR and HER catalytic activity of TM@Mo<sub>2</sub>B<sub>2</sub> at the embedded transition metal site (site I), Mo atoms on the surface around the TM (site II, III and IV), B atoms on the bridge sites (site V and VI) and Mo atom on the bridge sites (site VII).

#### 3.2 Electronic properties

Electrical conductivity is vital for electrocatalysts to guarantee electron transfer efficiency during the electrocatalytic reactions. On account of this, the electronic properties of the pristine Mo<sub>2</sub>B<sub>2</sub>, Mo<sub>2</sub>B<sub>2</sub> with Mo monovacancies (Mo<sub>2</sub>B<sub>2</sub>-V<sub>Mo</sub>) and TM@Mo<sub>2</sub>B<sub>2</sub> were investigated. Fig. 2 shows the total density of states (TDOS) and projected density of states (PDOS), of Mo<sub>2</sub>B<sub>2</sub>, Mo<sub>2</sub>B<sub>2</sub>-V<sub>Mo</sub>, Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub> (the other TM@Mo<sub>2</sub>B<sub>2</sub> are depicted in Fig. S2<sup>†</sup>). Obviously, the pristine Mo<sub>2</sub>B<sub>2</sub> exhibits metallic conductivity with the Fermi energy falling into a continuum of energy states, which is consistent with previous work.<sup>30</sup> Meanwhile, Mo<sub>2</sub>B<sub>2</sub>-V<sub>Mo</sub>, Ni@Mo<sub>2</sub>B<sub>2</sub>, Cu@Mo<sub>2</sub>B<sub>2</sub> and all the TM@Mo<sub>2</sub>B<sub>2</sub> are metallic. According to the projected density of states (PDOS), the metallic conductivity of the studied materials is mainly contributed by the Mo-4d orbitals near their Fermi levels.

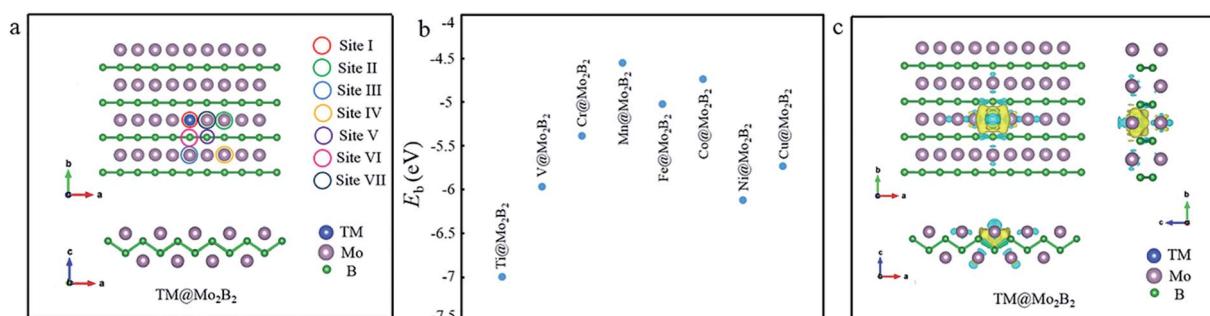


Fig. 1 (a) The structure and seven possible active sites of TM@Mo<sub>2</sub>B<sub>2</sub>. (b) The binding energy diagram of different TM@Mo<sub>2</sub>B<sub>2</sub> (TM = Ti, V, Cr, Mn, Fe, Co, Ni and Cu). (c) The charge density difference of TM@Mo<sub>2</sub>B<sub>2</sub>, where yellow and blue regions indicate the charge density accumulation and depletion, respectively.

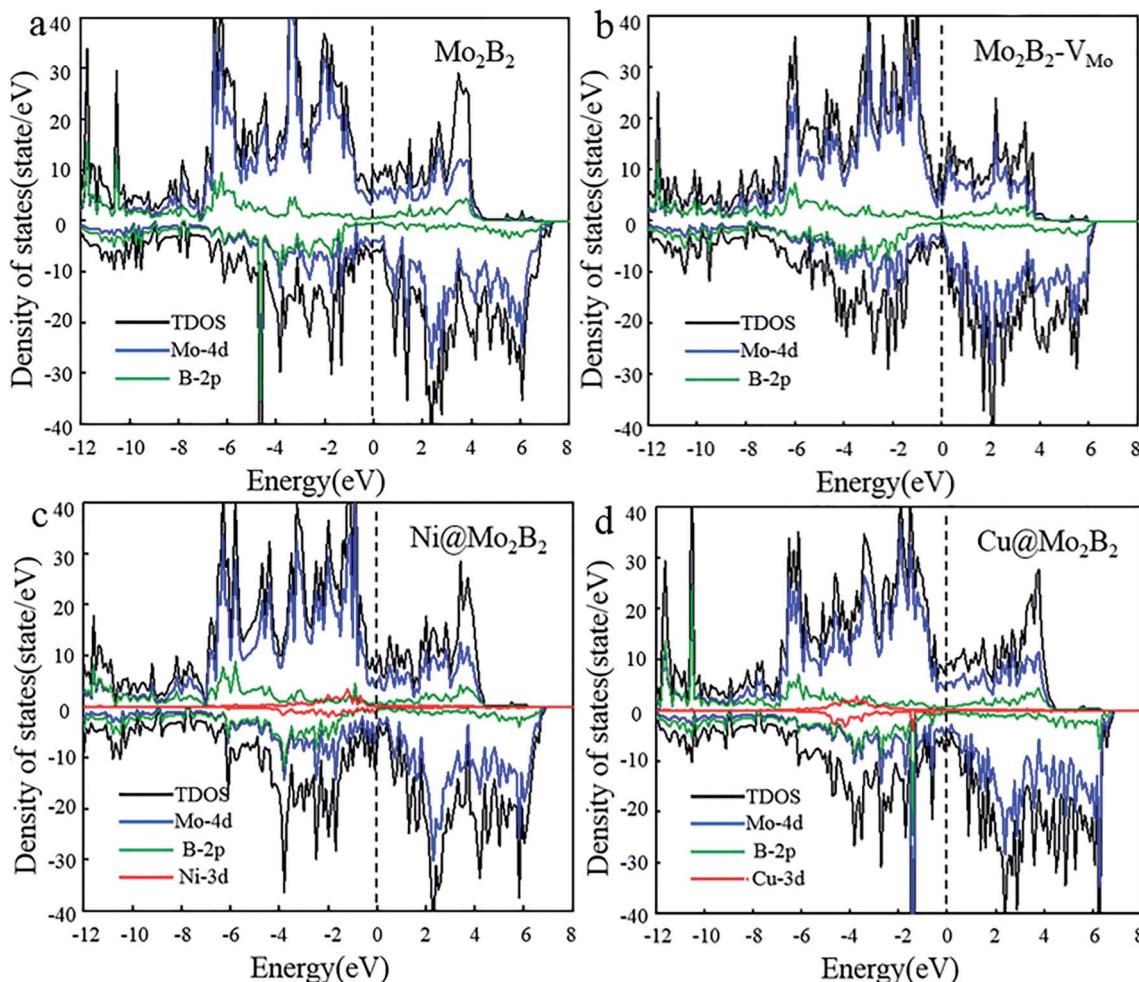


Fig. 2 The total density of states (TDOS) and the projected density of states (PDOS) of (a) pristine  $\text{Mo}_2\text{B}_2$ , (b)  $\text{Mo}_2\text{B}_2\text{-V}_{\text{Mo}}$ , (c)  $\text{Ni}@\text{Mo}_2\text{B}_2$  and (d)  $\text{Cu}@\text{Mo}_2\text{B}_2$ , where the Fermi level is set to 0 eV.

### 3.3 OER and ORR catalytic activity

After verifying the stability and electrical conductivity of TM@ $\text{Mo}_2\text{B}_2$ , we studied the catalytic activity of TM@ $\text{Mo}_2\text{B}_2$  for the OER and ORR. As depicted in Fig. 3, there are four elementary steps of the OER, which is also the inverse process of the ORR. Firstly, we studied which of the four sites mentioned above is the active site for the OER and ORR. As listed in Tables S2–S15,<sup>†</sup> for  $\text{Ti}@\text{Mo}_2\text{B}_2$ ,  $\text{V}@\text{Mo}_2\text{B}_2$ ,  $\text{Fe}@\text{Mo}_2\text{B}_2$ ,  $\text{Co}@\text{Mo}_2\text{B}_2$ ,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  in the OER, site I is the optimal active site with a lower overpotential than that of the other six sites, while for  $\text{Cr}@\text{Mo}_2\text{B}_2$  and  $\text{Mn}@\text{Mo}_2\text{B}_2$  in the OER, site III is the optimal active site with a lower overpotential than that of the other six sites. In addition, for  $\text{Co}@\text{Mo}_2\text{B}_2$ ,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  in the ORR, site I is the optimal active site with a lower overpotential than that of the other six sites, while for  $\text{Ti}@\text{Mo}_2\text{B}_2$ ,  $\text{V}@\text{Mo}_2\text{B}_2$  and  $\text{Cr}@\text{Mo}_2\text{B}_2$  in the ORR, site IV is the optimal active site with a lower overpotential than that of the other six sites, and for  $\text{Mn}@\text{Mo}_2\text{B}_2$  and  $\text{Fe}@\text{Mo}_2\text{B}_2$  in the ORR, site VI is the optimal active site with a lower overpotential than that of the other six sites.

For the OER, we calculated the Gibbs free energy change for each elementary reaction to draft the Gibbs free energy diagrams, as shown in Fig. 4 and Fig. S3.<sup>†</sup> From the free energy diagrams, we can see that for  $\text{Ti}@\text{Mo}_2\text{B}_2$ ,  $\text{V}@\text{Mo}_2\text{B}_2$ ,  $\text{Cr}@\text{Mo}_2\text{B}_2$ ,  $\text{Mn}@\text{Mo}_2\text{B}_2$ ,  $\text{Fe}@\text{Mo}_2\text{B}_2$ ,  $\text{Co}@\text{Mo}_2\text{B}_2$  and  $\text{Ni}@\text{Mo}_2\text{B}_2$ , the third step of  $\text{O}^*$  reacting with  $\text{H}_2\text{O}$  to form  $\text{OOH}^*$  is the most energy-consuming step of the entire OER with  $\Delta G_3$  values of 3.86, 3.80, 3.32, 2.84, 2.26, 2.13 and 1.75 eV, respectively. In the OER process with  $\text{Cu}@\text{Mo}_2\text{B}_2$  as the catalyst, the step of  $\text{OH}^*$  dissociating to  $\text{H}^+$  and  $\text{O}^*$  (the second step), is the most energy-consuming step and  $\Delta G_2$  is 1.54 eV. In addition, we calculated the overpotential for TM@ $\text{Mo}_2\text{B}_2$  which is the most important indicator to determine the OER performance.  $\text{Ni}@\text{Mo}_2\text{B}_2$  ( $\eta_{\text{OER}} = 0.52$  V) has better catalytic performance for the OER with a lower overpotential than that of  $\text{IrO}_2$  ( $\eta_{\text{OER}} = 0.56$  V).<sup>49</sup> It is worth noting that the overpotential for  $\text{Cu}@\text{Mo}_2\text{B}_2$  ( $\eta_{\text{OER}} = 0.31$  V) is the lowest in this work, even lower than that of the state-of-the-art  $\text{IrO}_2$  ( $\eta_{\text{OER}} = 0.56$  V) and  $\text{RuO}_2$  ( $\eta_{\text{OER}} = 0.42$  V),<sup>49</sup> indicating that the OER catalytic activity of  $\text{Cu}@\text{Mo}_2\text{B}_2$  is better than that of  $\text{IrO}_2$  and  $\text{RuO}_2$ . Furthermore, it is notable that for the pristine  $\text{Mo}_2\text{B}_2$ ,  $\eta_{\text{OER}}$  was calculated to be 2.67 V, as listed in

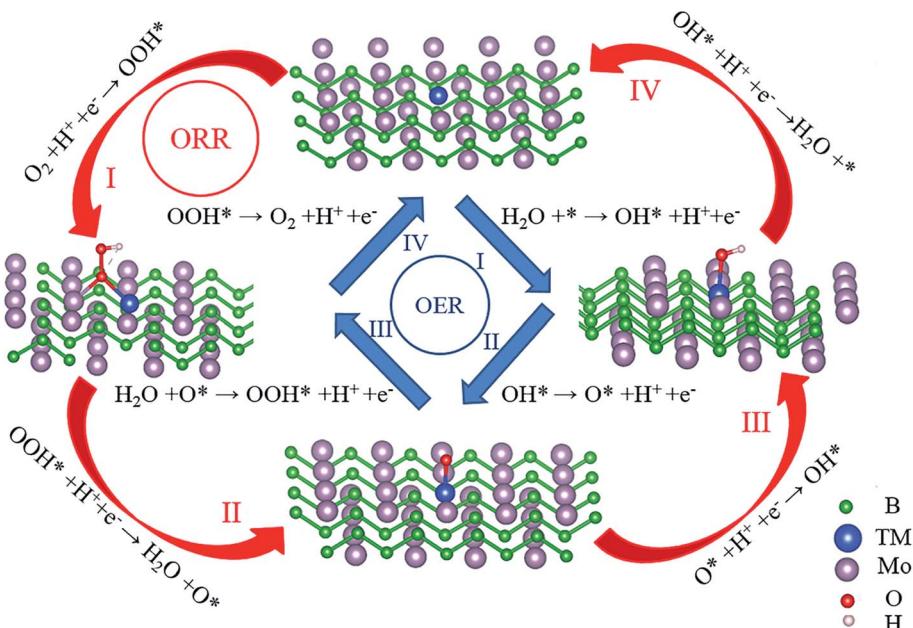


Fig. 3 Elementary reaction steps of the OER and ORR process for TM@Mo<sub>2</sub>B<sub>2</sub> at site I.

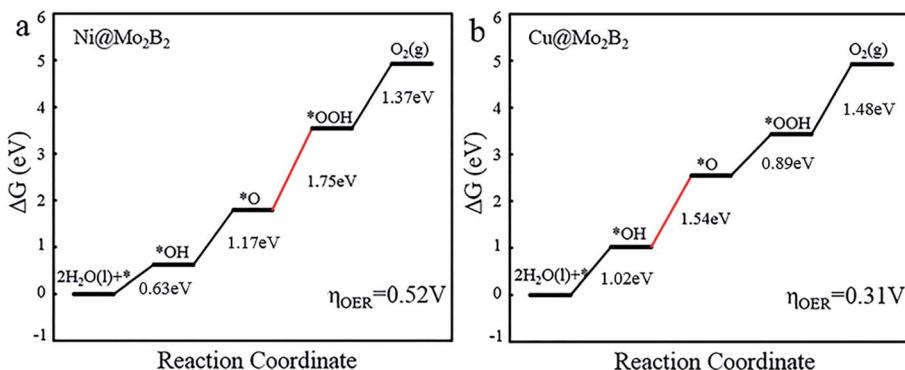


Fig. 4 The Gibbs free energy diagrams for the OER pathway of (a) Ni@Mo<sub>2</sub>B<sub>2</sub> and (b) Cu@Mo<sub>2</sub>B<sub>2</sub> at site I, where the red lines represent the most energy-consuming step of the OER.

Table S16.† Based on the above results, we can conclude that the OER catalytic activity of Mo<sub>2</sub>B<sub>2</sub> MBene is significantly improved after embedding with the above transition metal atoms.

Next, we further evaluated the reaction mechanism for the ORR. Generally, there are two possible reaction mechanisms for the ORR in acidic media, *i.e.*, the associative and dissociative mechanism, the difference of which depends on whether the adsorbed O<sub>2</sub> molecule on the catalytic site can be dissociated into two separate O atoms. If so, it is the dissociative pathway, otherwise it is the associative pathway. Before calculating the dissociation barrier, we studied the most stable O<sub>2</sub> adsorption configuration. It is found that the O<sub>2</sub> adsorption energy for the end-on configuration is 7.93 eV lower than that for the side-on configuration, indicating that O<sub>2</sub> prefers to adsorb on Cu@Mo<sub>2</sub>B<sub>2</sub> with the end-on configuration. As shown in Fig. S7,† by calculating the dissociation barrier of the adsorbed O<sub>2</sub> molecule at site I of Cu@Mo<sub>2</sub>B<sub>2</sub> to form two separate O<sup>\*</sup>, we can

find that the dissociation process for Cu@Mo<sub>2</sub>B<sub>2</sub> would overcome a large energy barrier of 7.94 eV, which is higher than the associative barrier (0.07 eV, Fig. S6 (a)†). Therefore, in this work, we research the associative pathway for the ORR, rather than the dissociative pathway.

The Gibbs free energy diagrams of the ORR process are presented in Fig. 5 and Fig. S4.† It is obvious that for Ti@Mo<sub>2</sub>B<sub>2</sub>, V@Mo<sub>2</sub>B<sub>2</sub>, Cr@Mo<sub>2</sub>B<sub>2</sub>, Mn@Mo<sub>2</sub>B<sub>2</sub>, Fe@Mo<sub>2</sub>B<sub>2</sub>, Co@Mo<sub>2</sub>B<sub>2</sub> and Ni@Mo<sub>2</sub>B<sub>2</sub> at site I, the fourth step of OH<sup>\*</sup> reacting with H<sup>+</sup> to form H<sub>2</sub>O is the most energy-consuming step of the entire ORR with  $\Delta G_d$  values of 1.32, 0.98, 1.29, -0.44, 0.45, -0.16 and -0.63 eV, respectively, while for Cu@Mo<sub>2</sub>B<sub>2</sub>, the most energy-consuming step is the second step, that is, the step of OOH<sup>\*</sup> reacting with H<sup>+</sup> to form H<sub>2</sub>O and O<sup>\*</sup> ( $\Delta G_b$  are -0.89 eV). Importantly, Cu@Mo<sub>2</sub>B<sub>2</sub> has the lowest overpotential ( $\eta_{ORR} = 0.34\text{ V}$ ) for the ORR among all the studied TM@Mo<sub>2</sub>B<sub>2</sub>, which is even lower than that of Pt ( $\eta_{ORR} = 0.45\text{ V}$ ). Hence, Cu@Mo<sub>2</sub>B<sub>2</sub>

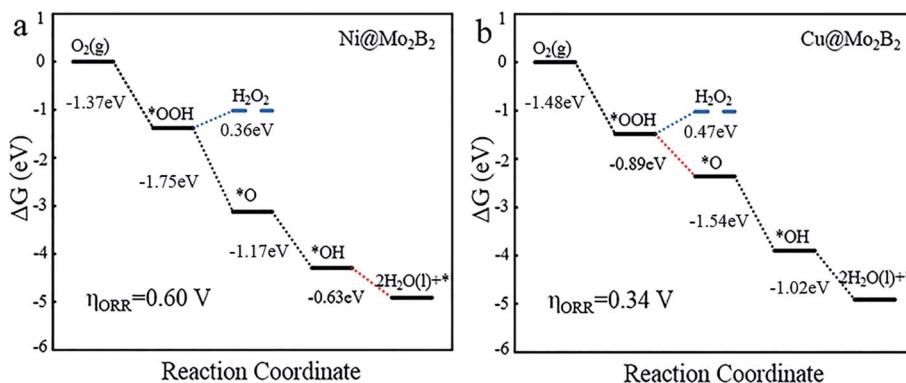


Fig. 5 The Gibbs free energy diagrams for the  $4e^-$  and  $2e^-$  ORR processes of (a)  $\text{Ni}@\text{Mo}_2\text{B}_2$  and (b)  $\text{Cu}@\text{Mo}_2\text{B}_2$  at site I, where the blue lines represent the  $2e^-$  ORR process, the black lines represent the  $4e^-$  ORR process, and the red dashed lines represent the most energy-consuming step of the ORR.

also exhibits good ORR catalytic activity apart from OER activity. Similarly, we computed the overpotential of pristine  $\text{Mo}_2\text{B}_2$  for the ORR, as listed in Table S16,<sup>†</sup> and the result ( $\eta_{\text{ORR}} = 1.50$  V) indicates that the ORR performance for pristine  $\text{Mo}_2\text{B}_2$  is greatly improved by embedding Mn, Co, Ni and Cu. In terms of kinetics, for the four elementary steps of the ORR proceeding on  $\text{Cu}@\text{Mo}_2\text{B}_2$ , the whole process is kinetically favorable, as shown in Fig. S6.<sup>†</sup> The third electron transfer step ( $\text{O}^*$  reacting with  $\text{H}^+$  to form  $\text{OH}^*$ ) is the rate-limiting step with a moderate activation energy barrier of 0.75 eV. For the reverse process of the ORR, *i.e.*, the OER, the third electron transfer step ( $\text{O}^*$  reacting with  $\text{H}_2\text{O}$  to form  $\text{OOH}^*$  and  $\text{H}^+$ ) is the rate-limiting step with an activation energy barrier of 1.04 eV.

The most energy-consuming steps of the OER and ORR are both the third steps ( $\Delta G_3 = 3.9$  eV,  $\Delta G_c = 0.27$  eV) for  $\text{Mo}_2\text{B}_2$ . However,  $\Delta G_3$  decreases to 1.75 and 0.89 eV while  $\Delta G_c$  decreases to  $-1.17$  and  $-1.54$  eV for  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ , respectively, indicating that the catalytic activity of  $\text{Mo}_2\text{B}_2$  is enhanced after embedding Ni or Cu. It is found that the valence state of Mo atoms is  $+0.61$  in bare  $\text{Mo}_2\text{B}_2$ , while the valence states of Ni and Cu are only  $+0.22$  and  $+0.20$  in  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ , respectively. The large positive net charges (high valence states) of Mo atoms result in strong adsorption between  $\text{O}^*$  and the adjacent Mo atom in bare  $\text{Mo}_2\text{B}_2$ , leading to large  $\Delta G_3$  and  $\Delta G_c$ . However, the bonding strength between  $\text{O}^*$  and Ni/Cu atoms is moderate due to the relatively small positive net charges (low valence states) of Ni/Cu, contributing to decreased  $\Delta G_3$  and  $\Delta G_c$  in  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ .

In addition, from  $\text{OOH}^*$ , there are several pathways to proceed, such as to form  $\text{O}^*$ ,  $\text{HOOH}$  or  $\text{OH}^* + \text{OH}^*$ . Notably, in acidic media, the  $2e^-$  reduction process forming  $\text{HOOH}$  is the competitive side reaction of the  $4e^-$  reduction process, which consists of the following steps:



To reveal the competitive relationship between the  $4e^-$  and  $2e^-$  processes, we plotted the Gibbs free energy diagrams of the

two different processes for  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ . As shown in Fig. 5, in the  $2e^-$  process,  $\Delta G$  of the second elementary reaction of the  $2e^-$  reduction process (eqn (18)) is 0.36 and 0.47 eV for  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ , respectively, which are both positive. However, in the  $4e^-$  process, the  $\Delta G_b$  values are  $-1.75$  and  $-0.89$  eV for  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$ , respectively, which are both negative. Therefore,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  are highly selective for the  $4e^-$  process forming  $\text{H}_2\text{O}$  rather than the  $2e^-$  process forming  $\text{H}_2\text{O}_2$ . Furthermore, as displayed in Fig. S5,<sup>†</sup> for  $\text{Ni}@\text{Mo}_2\text{B}_2$ ,  $\Delta G$  values from  $\text{OOH}^*$  to  $\text{OH}^* + \text{OH}^*$  (0.29 eV) or  $\text{OH}^* + \text{O}^*$  (0.17 eV) are all positive. However,  $\Delta G_b$  is  $-1.75$  eV for  $\text{Ni}@\text{Mo}_2\text{B}_2$ . Hence,  $\text{Ni}@\text{Mo}_2\text{B}_2$  tends to the pathway from  $\text{OOH}^*$  to  $\text{O}^*$  rather than from  $\text{OOH}^*$  to  $\text{OH}^* + \text{OH}^*$  or  $\text{OH}^* + \text{O}^*$ . For  $\text{Cu}@\text{Mo}_2\text{B}_2$ ,  $\Delta G$  from  $\text{OOH}^*$  to  $\text{OH}^* + \text{OH}^*$  ( $-0.20$  eV) is negative, but  $\Delta G_b$  from  $\text{OOH}^*$  to  $\text{O}^*$  ( $-0.89$  eV) is more negative. In addition,  $\Delta G$  from  $\text{OOH}^*$  to  $\text{OH}^* + \text{O}^*$  (7.19 eV) is positive. Based on this,  $\text{Cu}@\text{Mo}_2\text{B}_2$  is highly selective for the pathway from  $\text{OOH}^*$  to  $\text{O}^*$  rather than that from  $\text{OOH}^*$  to  $\text{OH}^* + \text{OH}^*$ . Thus,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  also possess high selectivity for the process of forming  $\text{O}^*$  from  $\text{OOH}^*$ .

In previous work,<sup>5,14,26</sup> the Gibbs free energies ( $\Delta G_{\text{OH}^*}$ ,  $\Delta G_{\text{O}^*}$  and  $\Delta G_{\text{OOH}^*}$ ) of three intermediates have been considered as the possible descriptors for the binding strength between the active atoms of the catalyst and the intermediates. During the construction of free energy diagrams for  $\text{TM}@\text{Mo}_2\text{B}_2$ , a linear scaling relationship between  $\Delta G_{\text{OH}^*}$  and  $\Delta G_{\text{O}^*}$ ,  $\Delta G_{\text{OOH}^*}$  was observed. As shown in Fig. 6a,  $\Delta G_{\text{O}^*}$  showed strong linear correlation with  $\Delta G_{\text{OH}^*}$ , which can be described by the following expressions:  $\Delta G_{\text{O}^*} = 1.69\Delta G_{\text{OH}^*} + 0.74$  eV with a coefficient of determination ( $R^2$ ) of 0.972. However, the linear relationship between  $\Delta G_{\text{OOH}^*}$  and  $\Delta G_{\text{OH}^*}$  is not strong. Therefore,  $\Delta G_{\text{OH}^*}$  and  $\Delta G_{\text{OOH}^*}$  can be adopted as the descriptor for the binding strength between the active atoms of the catalyst and the intermediates. Based on the above relationship, a dual volcano plot for the ORR and OER was constructed, as shown in Fig. 6b. The dual volcano plot has unique advantages in describing the bifunctional activity for reversible OER/ORR processes (the strategy of the dual volcano plot is shown in the ESI<sup>†</sup>). When the OER and ORR

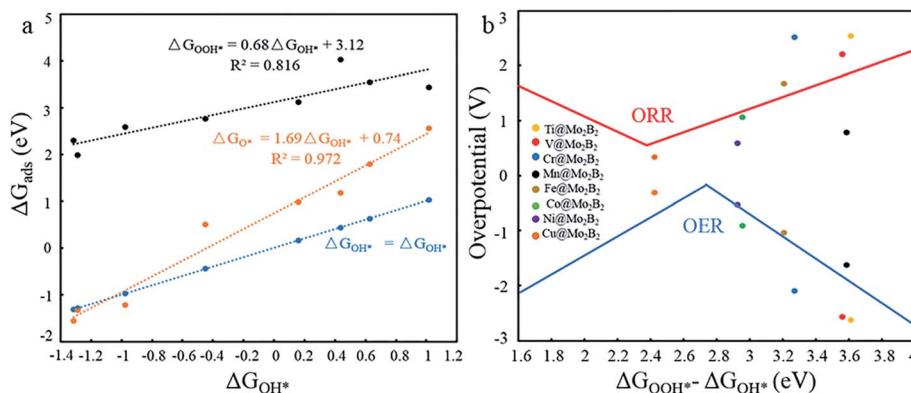


Fig. 6 (a) Scaling relationship between the  $\Delta G_{\text{OH}^*}$  and  $\Delta G_{\text{O}^*}$ ,  $\Delta G_{\text{OOH}^*}$  at site I. (b) Dual volcano plot for the OER and ORR for TM@Mo<sub>2</sub>B<sub>2</sub> at site I.

locate more to the right on the branch of the volcano plot, the OH\* binding strength is weaker. Located near the top of the OER volcano plot, Ni@Mo<sub>2</sub>B<sub>2</sub> possesses good OER catalytic activity. Also, it is worth mentioning that Cu@Mo<sub>2</sub>B<sub>2</sub> is at the top of both the OER and ORR volcano diagrams, indicating that Cu@Mo<sub>2</sub>B<sub>2</sub> possesses outstanding OER/ORR bifunctional catalytic activity. Based on the values of overpotential and the dual volcano plot for the OER and ORR, Ni@Mo<sub>2</sub>B<sub>2</sub> exhibits excellent OER ( $\eta_{\text{OER}} = 0.52$  V) catalytic performance at site I, while Cu@Mo<sub>2</sub>B<sub>2</sub> possesses superb catalytic activity for both the OER ( $\eta_{\text{OER}} = 0.31$  V) and ORR ( $\eta_{\text{ORR}} = 0.34$  V), which can be applied in fuel cells and metal-air batteries.

### 3.4 HER catalytic activity

Generally, the entire HER process can be formalized by a three-state diagram, which consists of the initial state H<sup>+</sup> + e<sup>-</sup>, the intermediate state H\* and the final product H<sub>2</sub>. Herein, we study the HER catalytic activity of TM@Mo<sub>2</sub>B<sub>2</sub> at four different sites by calculating the Gibbs free energy difference of the intermediate state H\* and the final product H<sub>2</sub> ( $\Delta G_{\text{H}}$ ), which is considered to be the most important descriptor of the HER catalytic activity. Generally, the HER catalytic activity is considered to be high if  $|\Delta G_{\text{H}}| < 0.2$  eV. The closer the value of  $|\Delta G_{\text{H}}|$  is to 0, the higher the HER catalytic activity is.  $\Delta G_{\text{H}}$  values of all the studied TM@Mo<sub>2</sub>B<sub>2</sub> at different sites under 1/16 hydrogen coverage conditions are listed in Table S18†. As shown in Fig. 7, the HER performance of TM@Mo<sub>2</sub>B<sub>2</sub> with high OER or ORR catalytic activity (Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub>) under 1/16 hydrogen coverage conditions was studied. We can conclude that Cu@Mo<sub>2</sub>B<sub>2</sub> shows poor HER catalytic activity at site I, site II, site IV and site VII, while Ni@Mo<sub>2</sub>B<sub>2</sub> exhibits high HER catalytic activity at site I, site II and site IV. For comparison, we also conducted the HER catalytic activity test of the pristine Mo<sub>2</sub>B<sub>2</sub>, and its  $|\Delta G_{\text{H}}|$  is 0.37 eV, indicating that embedding Ni in Mo vacancies of Mo<sub>2</sub>B<sub>2</sub> MBenes improves the HER catalytic activity of Mo<sub>2</sub>B<sub>2</sub>. In addition, we further calculated the  $\Delta G_{\text{H}}$  of Ni@Mo<sub>2</sub>B<sub>2</sub> under different H coverage at site I, as shown in Table S20†. The calculated  $\Delta G_{\text{H}}$  for Ni@Mo<sub>2</sub>B<sub>2</sub> is -0.09 and 0.12 eV for hydrogen coverages of 1/4 and 1/9, respectively, indicating that under higher hydrogen coverages,

Ni@Mo<sub>2</sub>B<sub>2</sub> still exhibits high HER catalytic activity at site I. Among them, under 1/4 hydrogen coverage conditions, Ni@Mo<sub>2</sub>B<sub>2</sub> exhibits high HER catalytic activity compared with Pt (0.09 eV).<sup>11</sup> Considering the values of  $\Delta G_{\text{H}}$  and overpotential, Ni@Mo<sub>2</sub>B<sub>2</sub> possesses excellent HER and OER ( $\eta_{\text{OER}} = 0.52$  V) catalytic activity at site I and can be applied in water splitting.

Based on the above research, we can conclude that Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub> possess high catalytic activity with lower overpotential than the traditional catalysts for a single reaction. In addition, the two electrocatalysts in our work have exhibited extremely high bifunctional catalytic activity so far. For Ni@Mo<sub>2</sub>B<sub>2</sub>, the overpotential of the HER/OER is -0.09/0.52 V, respectively, indicating better HER/OER catalytic performance than that of Cu<sub>3</sub>(HITP)<sub>2</sub> (-0.02/0.75 V)<sup>14</sup> and Mn-anchored C<sub>2</sub>N (-0.15/0.67 V).<sup>5</sup> In particular, the overpotential of the OER/ORR for Cu@Mo<sub>2</sub>B<sub>2</sub> (0.31/0.34 V) is much lower than that for Co<sub>3</sub>(HITP)<sub>2</sub>, Fe<sub>3</sub>(HITP)<sub>2</sub>, Zn<sub>3</sub>(HITP)<sub>2</sub> (0.36/0.73 V, 0.83/0.59 V, and 0.89/0.52 V, respectively),<sup>14</sup> Co-doped g-C<sub>3</sub>N<sub>4</sub> (0.53/0.67 V),<sup>26</sup> Fe-based covalent organic framework (0.38/0.48 V)<sup>50</sup>

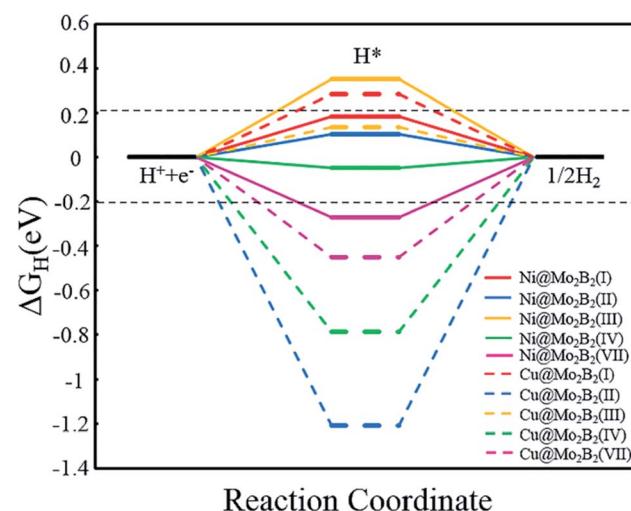


Fig. 7 Calculated Gibbs free energy diagram for the HER at different sites for Ni@Mo<sub>2</sub>B<sub>2</sub> and Cu@Mo<sub>2</sub>B<sub>2</sub> for a hydrogen coverage of 1/16. The two horizontal black dashed lines correspond to  $|\Delta G_{\text{H}}| = 0.2$  eV.

and  $\text{MoC}_2$  (0.45/0.47 V).<sup>9</sup> Therefore,  $\text{Ni}@\text{Mo}_2\text{B}_2$  and  $\text{Cu}@\text{Mo}_2\text{B}_2$  reported in this work are the best HER/OER and OER/ORR bifunctional catalysts so far.

## 4. Conclusions

In summary, we have demonstrated the feasibility of using  $\text{TM}@\text{Mo}_2\text{B}_2$  as HER/OER and OER/ORR bifunctional electrocatalysts by means of first-principles computations. With good structural stability and metallic conductivity, the OER, ORR and HER catalytic activity of  $\text{TM}@\text{Mo}_2\text{B}_2$  can be tailored by embedding different transition metals. In particular,  $\text{Ni}@\text{Mo}_2\text{B}_2$  is a promising HER/OER bifunctional electrocatalyst for overall water splitting with a low  $|\Delta G_{\text{H}}|$  (−0.09 eV) for the HER under 1/4 H coverage and overpotential (0.52 V) for the OER. Meanwhile,  $\text{Cu}@\text{Mo}_2\text{B}_2$  has the potential to be an OER/ORR bifunctional electrocatalyst characterized by low overpotentials for the OER and ORR (0.31 and 0.34 V, respectively) and can be compared with the best-known noble electrocatalysts. Our results indicate that  $\text{TM}@\text{Mo}_2\text{B}_2$  MBenes are expected to be economical and efficient candidates for HER/OER and OER/ORR bifunctional electrocatalysts applied in water splitting, fuel cells and metal-air batteries.

## Conflicts of interest

There are no conflicts to declare.

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