

Supplementary material

Electronic properties modulation for two-dimensional materials of boron phosphorus monolayer and derived single atom catalysts for the hydrogen evolution reaction

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Computational details about HER.

To evaluate the stability of the supported single atom catalysts (SACs), the binding energy (E_b) can be calculated by the following equation:

$$E_b(\text{TM}) = E_{\text{TM@sub}} - E_{\text{sub}} - E_{\text{TM}} \quad (\text{S1})$$

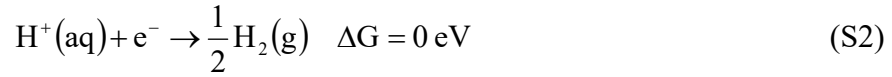
where $E_{\text{TM@sub}}$, E_{sub} and E_{TM} represent the total energies of TM@2D B_xN materials, 2D B_xN materials substrate and TM single atom, respectively. Generally, a negative

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E_b means stable binding of TM atom on B_xN materials surface, and a more negative value indicates a stronger bonding strength.

To evaluate the HER activity of SACs, the Gibbs free energy change (ΔG_{H^*}) of H adsorption is obtained using the method of Nørskov [1], where the hydrogenation process could be expressed as equation (S2):



Therefore, according to the Sabatier principle, the ΔG_{H^*} was a reliable descriptor to evaluate HER activity of catalysts [2]. It is well established that the ideal value for HER was $\Delta G_{H^*}=0$, that is, the absolute value of ΔG_{H^*} closes to zero, meaning the SACs own excellent catalytic activity and it was given in equation (S3):

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H + \Delta G(pH) \quad (S3)$$

ΔE_H is the differential hydrogen adsorption energy, which is obtained by:

$$\Delta E_H = E_{nH^*} - E_{(n-1)H^*} - \frac{1}{2} E_{H_2} \quad (S4)$$

E_{nH^*} and $E_{(n-1)H^*}$ describe the total energies of the 2D B_xN materials substrate with n and $(n-1)$ adsorbed hydrogen atom, respectively, while E_{H_2} is the total energy of a H_2 molecule in gas. ΔE_{ZPE} and ΔS_H are the correction of in zero-point energy and entropy change between the adsorbed H atom and $1/2 H_2$ in gas phase, respectively. Therefore, ΔE_{ZPE} is defined as:

$$\Delta E_{ZPE} = E_{ZPE}^{nH^*} - E_{ZPE}^{(n-1)H^*} - \frac{1}{2} E_{ZPE}^{H_2} \quad (S5)$$

where $E_{ZPE}^{nH^*}$ and $E_{ZPE}^{(n-1)H^*}$ are the zero-point energy of $(n+1)$ and n adsorbed H atoms on the TM@2D B_xN materials, respectively. The $E_{ZPE}^{H_2}$ is the zero-point energy of H_2 molecule in the gas phase. ΔS_H is defined as [3,4]:

$$\Delta S_H = \sum_{i=1}^{3N} \left[-R \ln \left(1 - e^{-\frac{h\nu_i}{T k_B}} \right) + \frac{N_A h \nu_i}{T} \frac{e^{-\frac{h\nu_i}{T k_B}}}{1 - e^{-\frac{h\nu_i}{T k_B}}} \right] - \frac{1}{2} S_{H_2} \quad (S6)$$

In general, ΔS_H is calculated as $\Delta S_H \approx -1/2 S_{H_2}$, which is approximately 0.20 eV when the value of pH is zero under standard conditions [5]. In this study, all calculations consider the HER occurs in all pH value.

At present, there has been controversy on the pH dependence of the catalytic activity [6-8]. Nevertheless, a thermochemical approach established by Nørskov et al. have predicted results in conformity to the experimental trends [2]. Therefore, this theoretical method is widely used to assess the pH dependent free energy barrier for H-adsorption on catalytic surfaces. On the basis of this theory, the entropy of hydrogen ion in an electrochemical process mainly depends on the pH. The effect of pH to ΔG_{H^*} is regarded as an additional entropic potential, then through the correction of entropy changes and vibration at 298.15 K, we can obtain the corrected Gibbs free energy change ($\Delta G(\text{pH})$) [9], using equation (S7):

$$\Delta G(\text{pH}) = \kappa_B T \ln(10) \times \text{pH} \quad (S7)$$

where $\Delta G(\text{pH})$ is closely in connection with the pH of the electrolyte and is an additional barrier for the H-adsorption. This simple expression as a function of pH values could be adopted to evaluate the catalytic performance of HER. Its essence is a thermodynamic estimate due to the change of the free energy of hydrogen ions in the electrolyte at different pH values. In equation (7), the value of $k_B T \ln(10)$ approximately equals to 5.92×10^{-2} eV at $T = 298.15$ K. At $\text{pH}=14$, $\Delta G(\text{pH})$ reaches a maximum value of 0.83 eV, which is in agreement with previous study (0.78 eV) [10].

Hence, the catalytic activity of SACs surface can be effectively improved by adjusting the pH of the electrolyte.

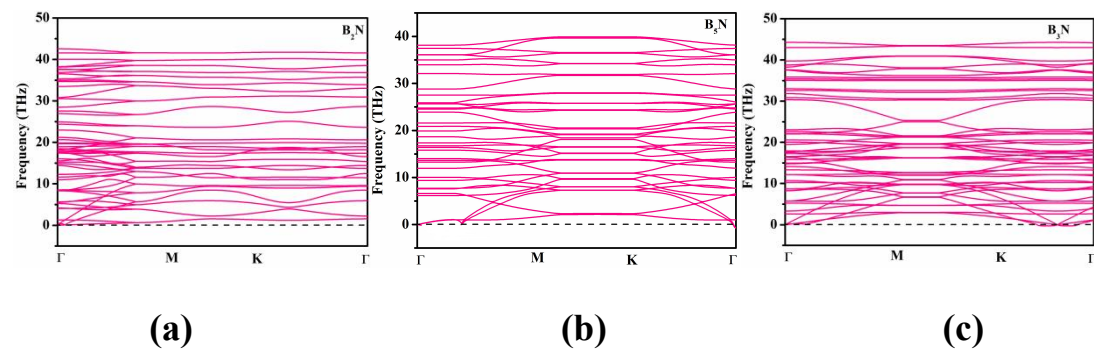


Fig. S1. Phonon band structure of the 2D (a) B_2N (b) B_3N and (c) B_5N monolayers.

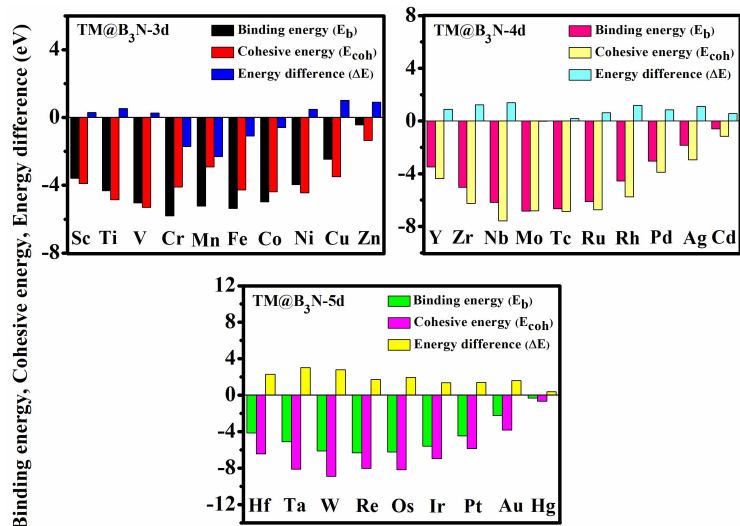


Fig. S2. The different TM atoms adsorption on the B_3N monolayer compounds and the corresponding binding energy (E_b), cohesive energy (E_{coh}) and their energy difference (ΔE).

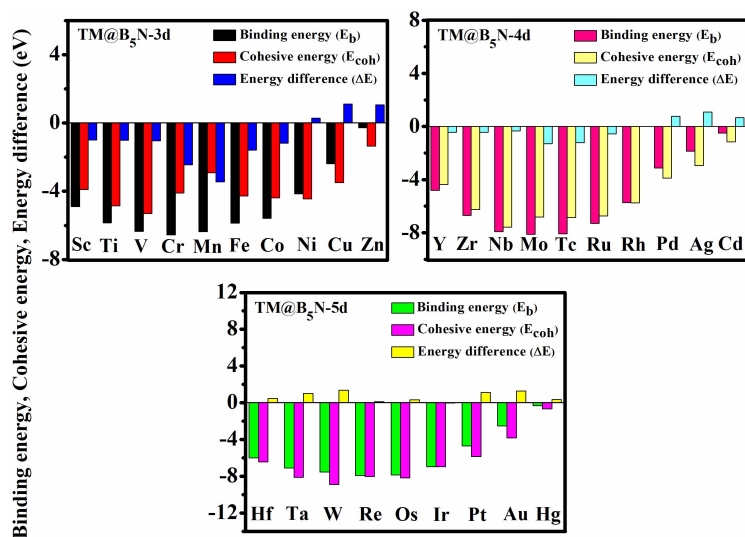
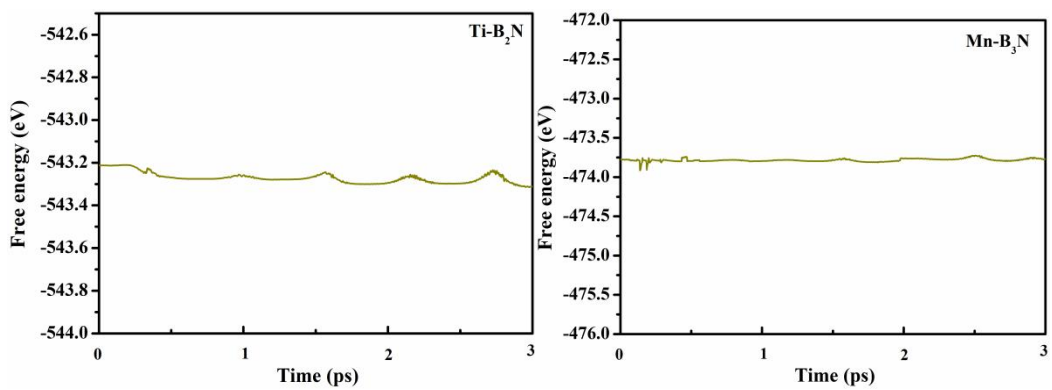
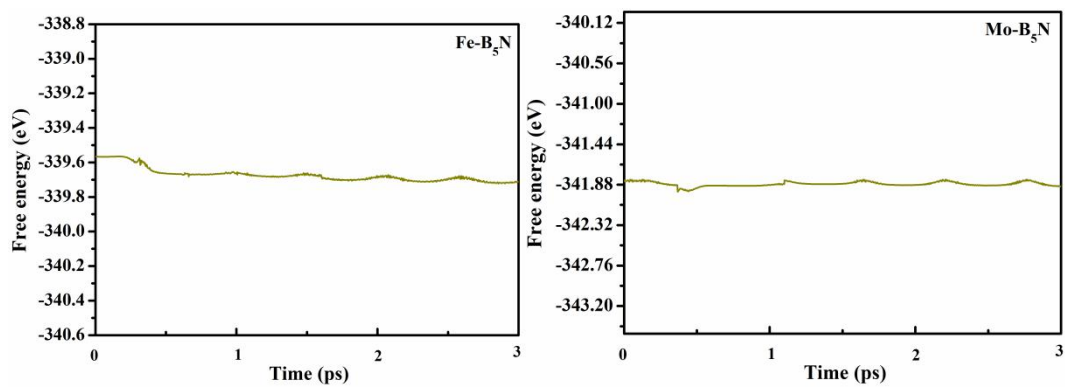


Fig. S3. The different TM atoms adsorption on the B_5N monolayer compounds and the corresponding binding energy (E_b), cohesive energy (E_{coh}) and their energy difference (ΔE).



(a)

(b)



(c)

(d)

Fig. S4. The fluctuation of total energy in AIMD simulations for Ti@B₂N, Mn@B₃N, Fe@B₅N and Mo@B₅N monolayers at 300 K.

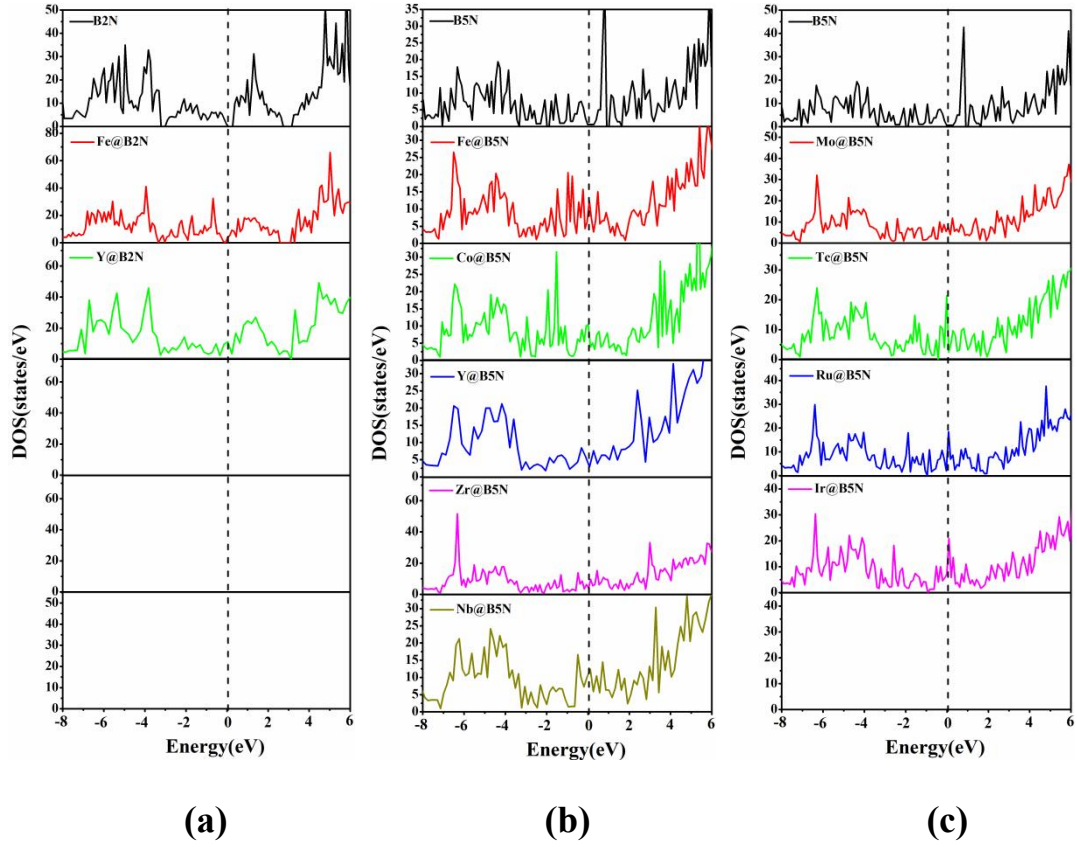
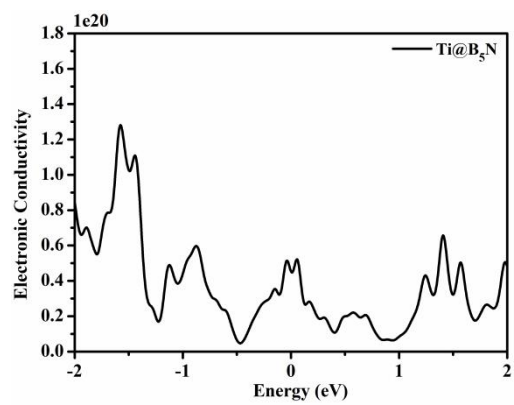
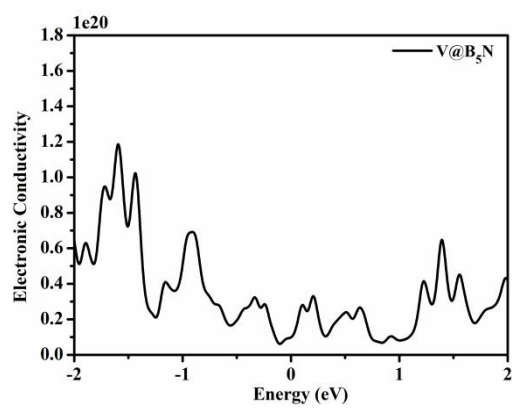


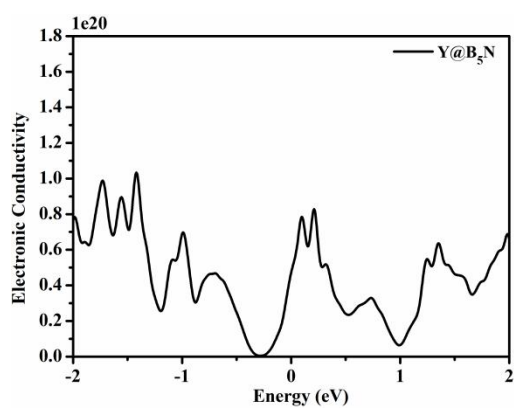
Fig. S5. The density of states (DOS) spectra for TM@B₂N, TM@B₃N and TM@B₅N. The Fermi levels are set to zero and indicated black dashed lines.



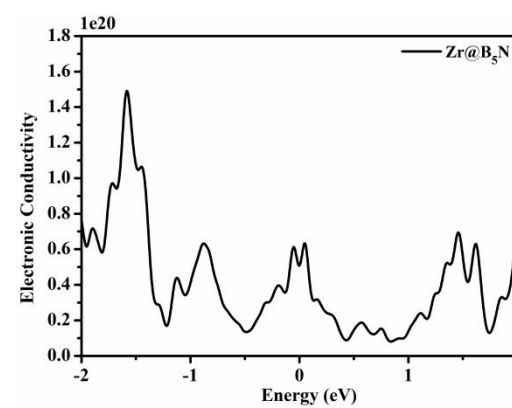
(a)



(b)



(c)



(d)

Fig. S6. The electronic conductivity variation of TM@B₅N SACs.

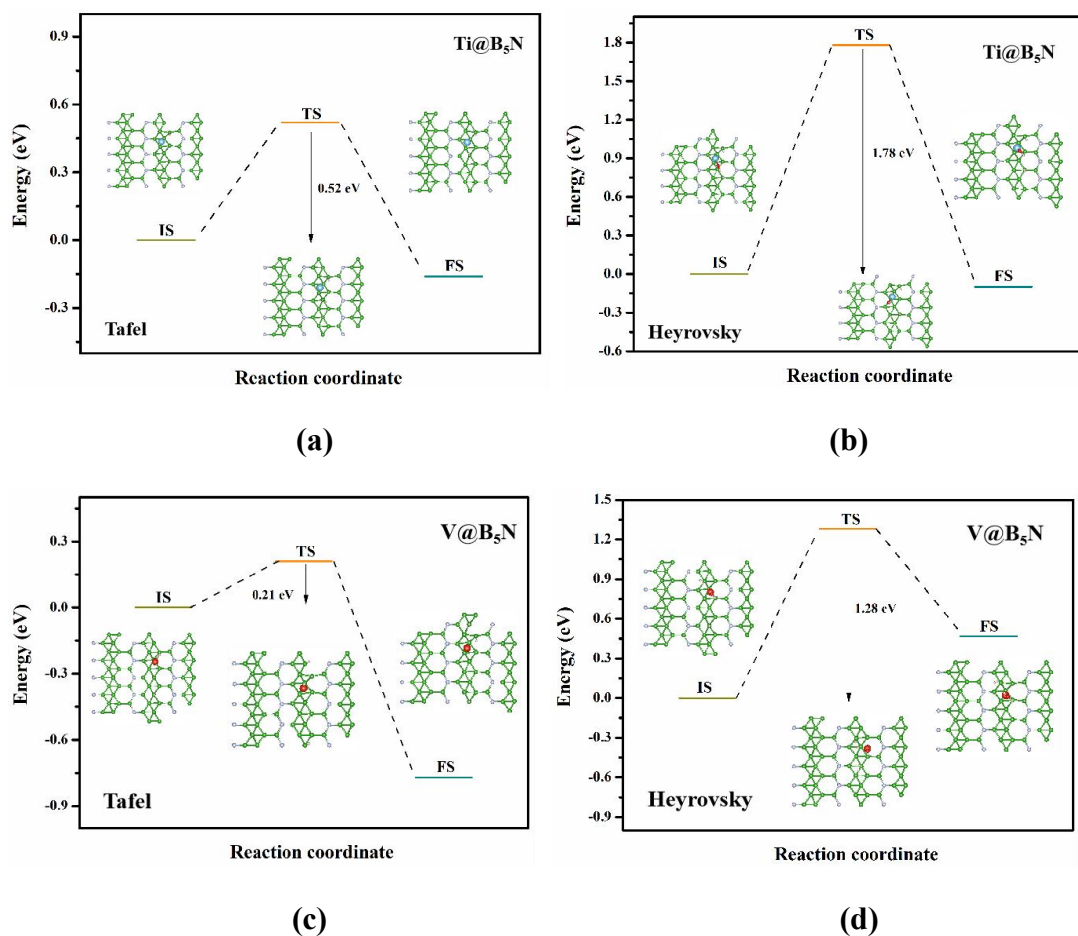


Fig. S7. Energy landscape of the Heyrovsky and the Tafel reactions on the (a-b) Ti@B₅N and (c-d)V@B₅N monolayers including the reaction coordinate structure of the initial state (IS), transition state (TS), and final state (FS).

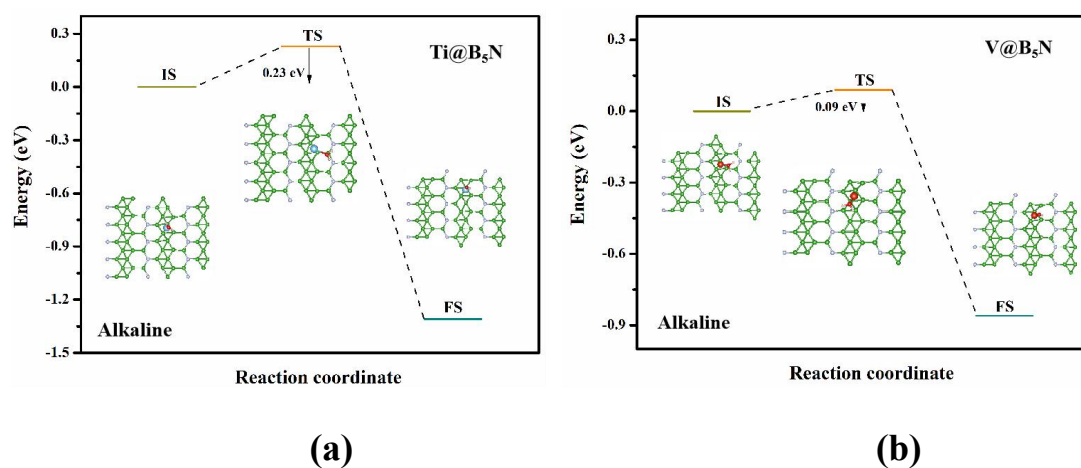


Fig. S8. Energy landscape of the water dissociation reaction on the Ti@B₅N and V@B₅N monolayers including the reaction coordinate structure of the initial state (IS), transition state (TS), and final state (FS).

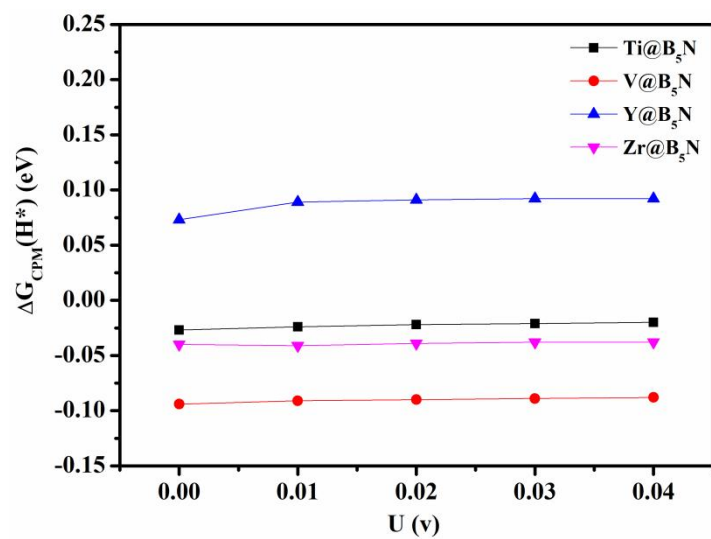


Fig. S9. Under the CPM model, the hydrogen adsorption free energy $\Delta G(\text{H}^*)$ on TM@B₅N SACs corresponding to different potentials.

Table S1. The different adsorption sites of TM atoms and the corresponding binding energy (E_b). Taking Sc@B₂N, Sc@B₃N and Sc@B₅N systems as examples.

System	Adsorption site	E_b (eV)
Sc@B ₂ N	B1 (Top site)	-4.07
	B2 (Top site)	-4.10
	B3 (Top site)	-4.60
	N (Top site)	-4.60
	H1 (Hollow site)	-4.75
Sc@B ₃ N	B1 (Top site)	-3.15
	B2 (Top site)	-3.81
	B3 (Top site)	-3.81
	B4 (Top site)	-3.75
	N (Top site)	-3.81
	H1 (Hollow site)	-3.59
	H2 (Hollow site)	-3.91
	H3 (Hollow site)	-3.75
Sc@B ₅ N	B1 (Top site)	-4.18
	B2 (Top site)	-5.15
	B3 (Top site)	-5.15
	B4 (Top site)	-5.16
	N (Top site)	-4.52
	H1 (Hollow site)	-4.18
	H2 (Hollow site)	-5.18

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