Supporting Information

Rational design of an efficient descriptor for single-atom catalysts in the hydrogen evolution reaction

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Note 1

The HER activity was evaluated by calculating the reaction free energy of each step based on the computational hydrogen electrode model [S1], in which the reaction:

$$H^+ + e^- \rightarrow \frac{1}{2}H_2$$

The Gibbs free energy of the adsorption of hydrogen (ΔG_{H^*}) was calculated by:

$$\Delta G_{H^*} = \Delta E_H + \Delta E_{ZPE} - T\Delta S_H$$

where ΔE_H is the hydrogen adsorption energy over different catalysts, which is defined as:

$$\Delta E_H = E_{H^*} - E_* - 1/2E_{H_2}$$

The ΔE_{ZPE} is the difference in the zero-point energy between the adsorbed state and the corresponding free-standing state, which can be obtained by:

$$\Delta E_{ZPE} = E_{ZPE}^{H} - \frac{1}{2}E_{ZPE}^{H_2}$$

The entropy is given by [S2]:

$$S(T) = \sum_{i=1}^{3N}[-R\ln(1-e^{-\frac{h\nu_i}{k_BT}}) + \frac{N_A h\nu_i}{T}\frac{e^{-h\nu_i/k_BT}}{1-e^{-h\nu_i/k_BT}}]$$

where R stands for the universal gas constant, k_B is the Boltzmann constant, h is Plank's constant, N_A is Avogadro's number, ν_i represents the frequency and N is the number of adsorbed atoms. Therefore, ΔG_{H^*} can be calculated as:

$$\begin{aligned}\Delta G_{H^*} &= \Delta E_H + \Delta E_{ZPE} - T\Delta S_H \\ &= \left(E_{H^*} + E_{ZPE(H^*)} - TS_{H^*}\right) - \frac{1}{2}\left(E_{H_2} + E_{ZPE(H_2)} - TS_{H_2}\right) - \left(E_* + E_{ZPE(*)} - TS_*\right) \\ &= \Delta E_H + 0.24\end{aligned}$$

In the Volcano curve, the exchange current (i_0) base on the Nørskov's assumption

[S1] is calculated by:

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

where k_0 is the rate constant. In general, the rate constants should be different for different systems. However, in the present calculations, the k_0 are set to 1 because there are no experimental data available. Actually, such treatment has been utilized and confirmed in many previous works [S3-S5], which is reasonable to understand the activity of different catalysts qualitatively.

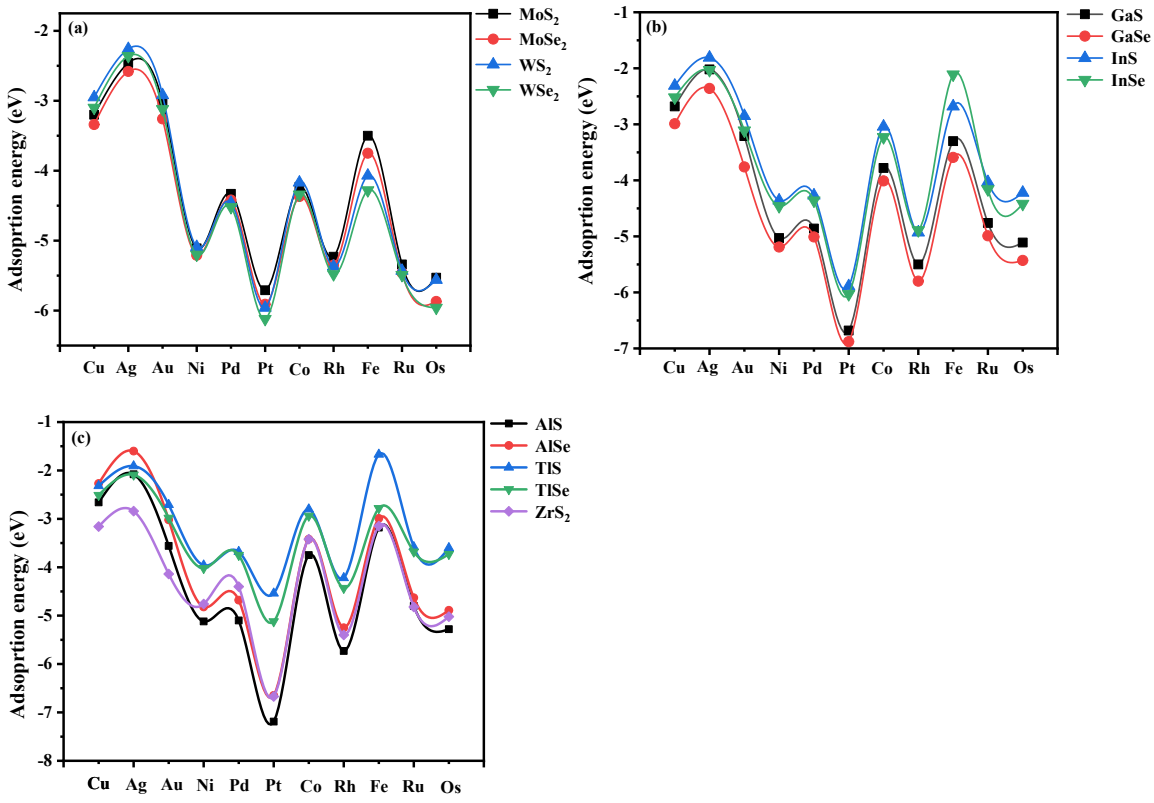
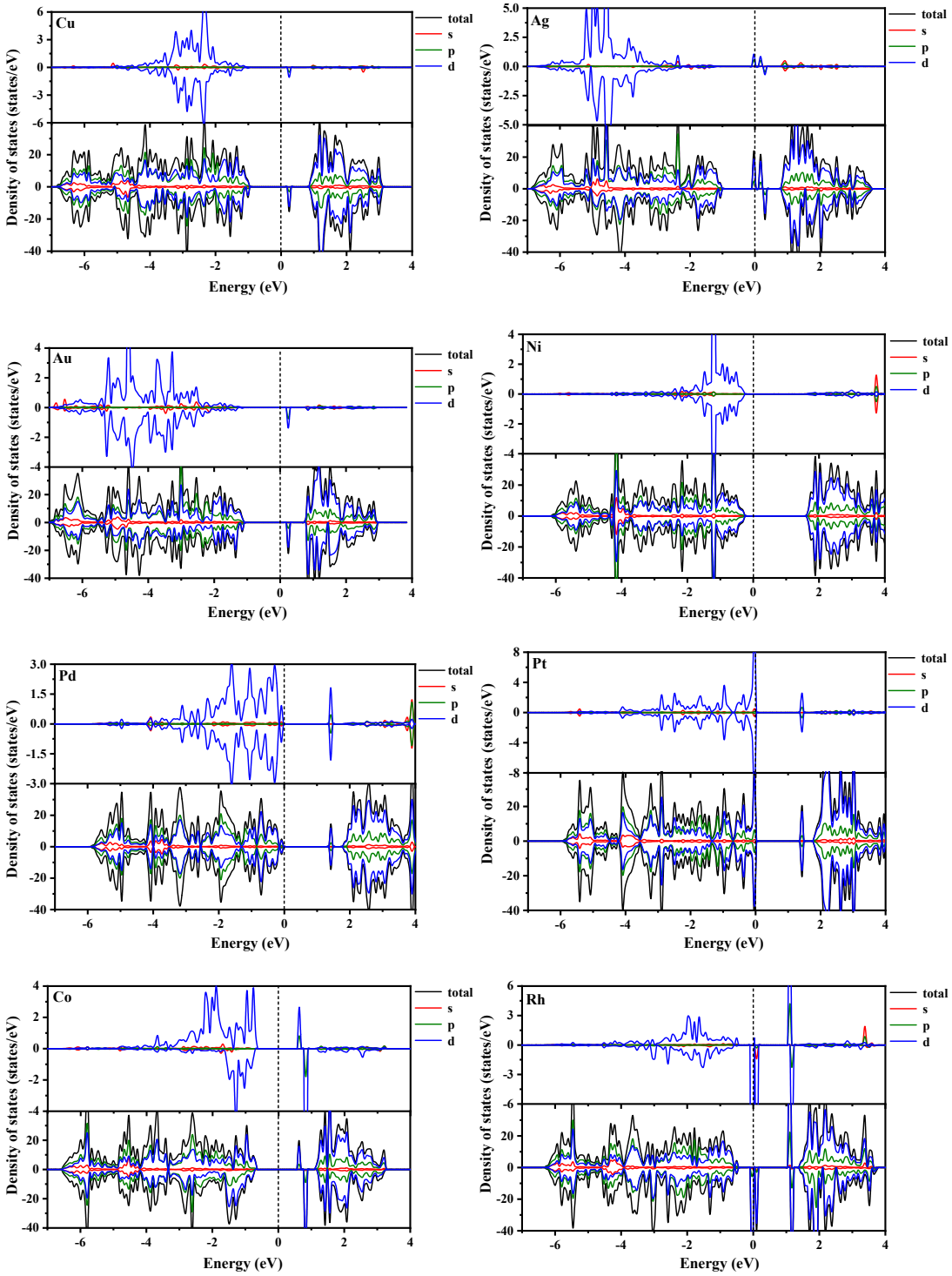


Fig. S1 Adsorption energies of different TM atoms on the substrates BX_2, AX and ZrS_2.


Cu
Ag
Au
Ni
Pd
Pt
Co
Rh
total
s
p
d
Density of states (states/eV)
Energy (eV)

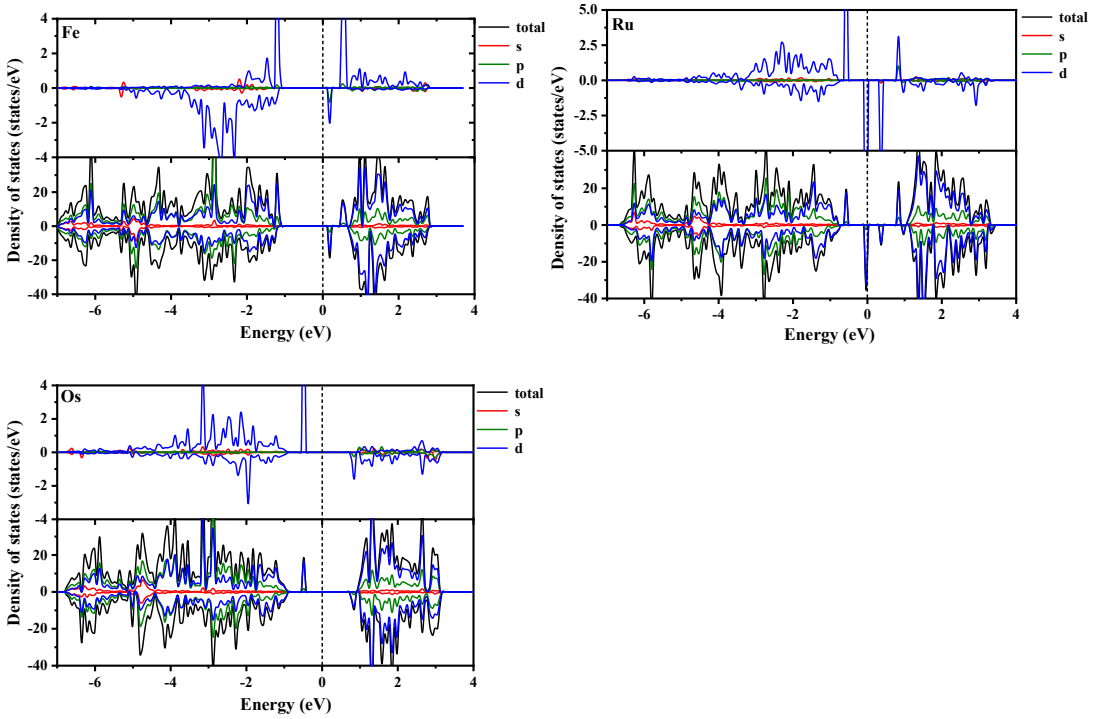


Fig. S2 Total and partial density of states of M-MoS_2.

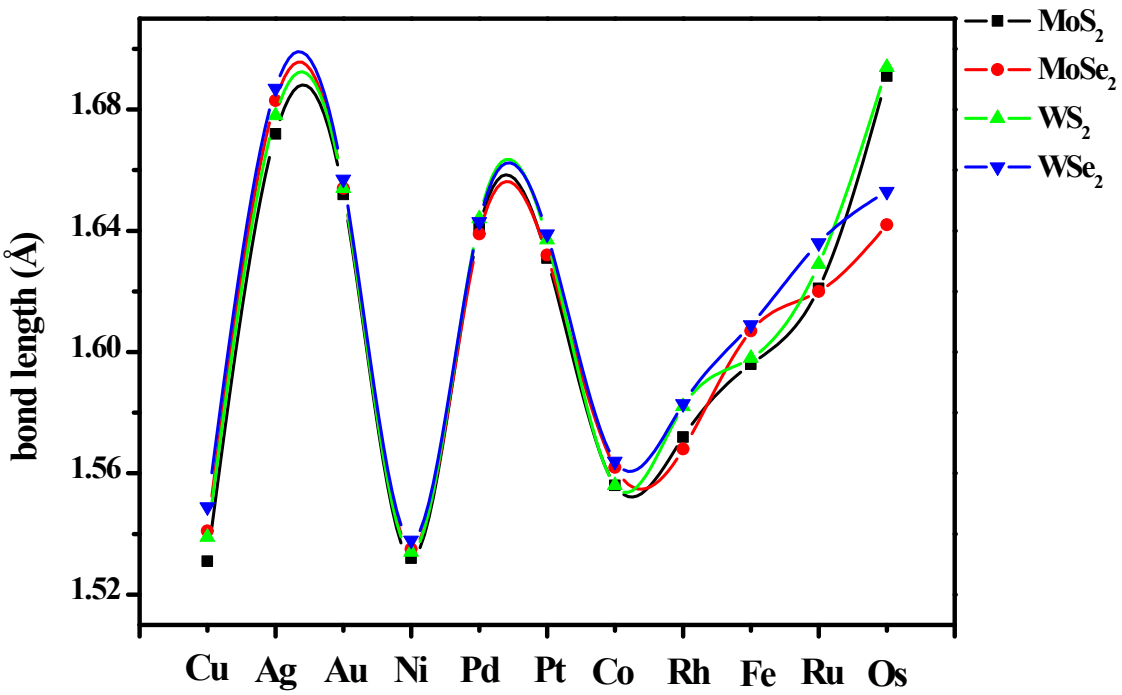


Fig. S3 Theoretical TM-H bond lengths of different TM atoms on the substrates BX_2.

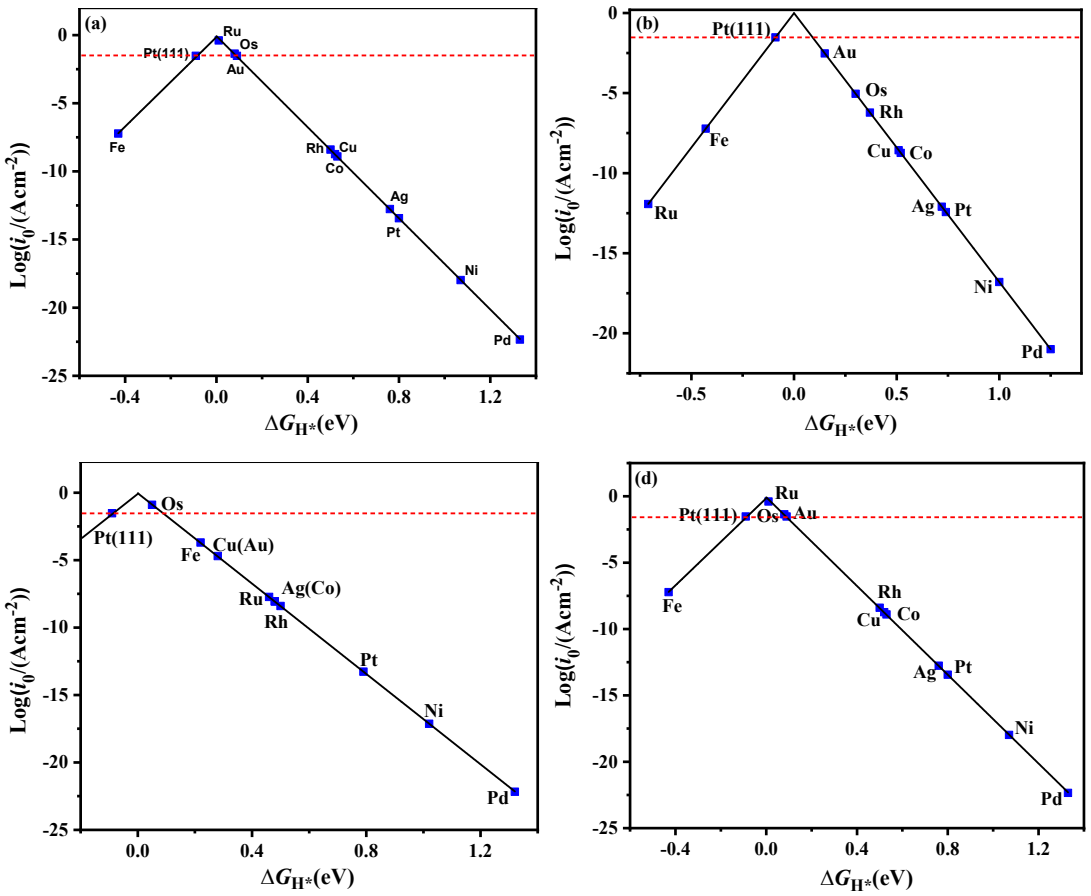


Fig. S4 Volcano curve of exchange current density i_0 as a function of the Gibbs free energy (ΔG_H*) of (a) MoS_2; (b) $MoSe_2$; (c) WS_2; (d) WSe_2.

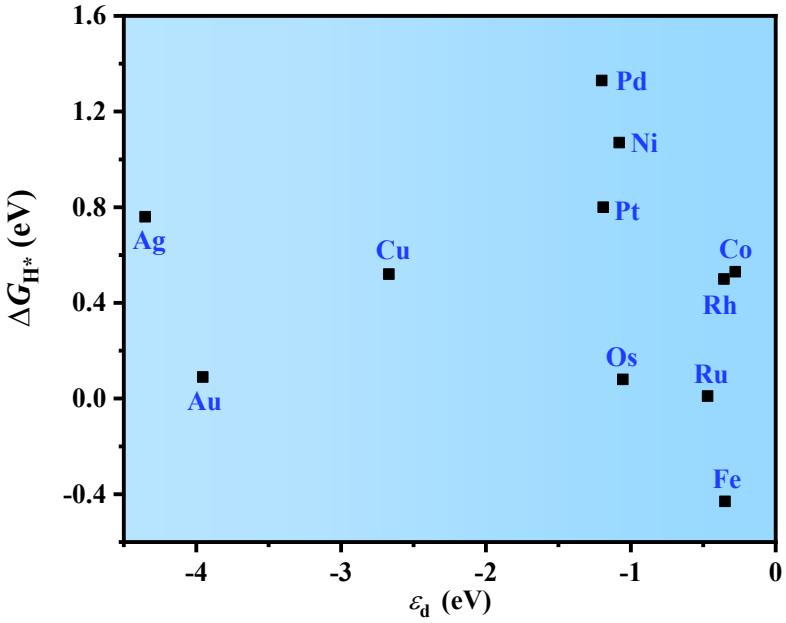
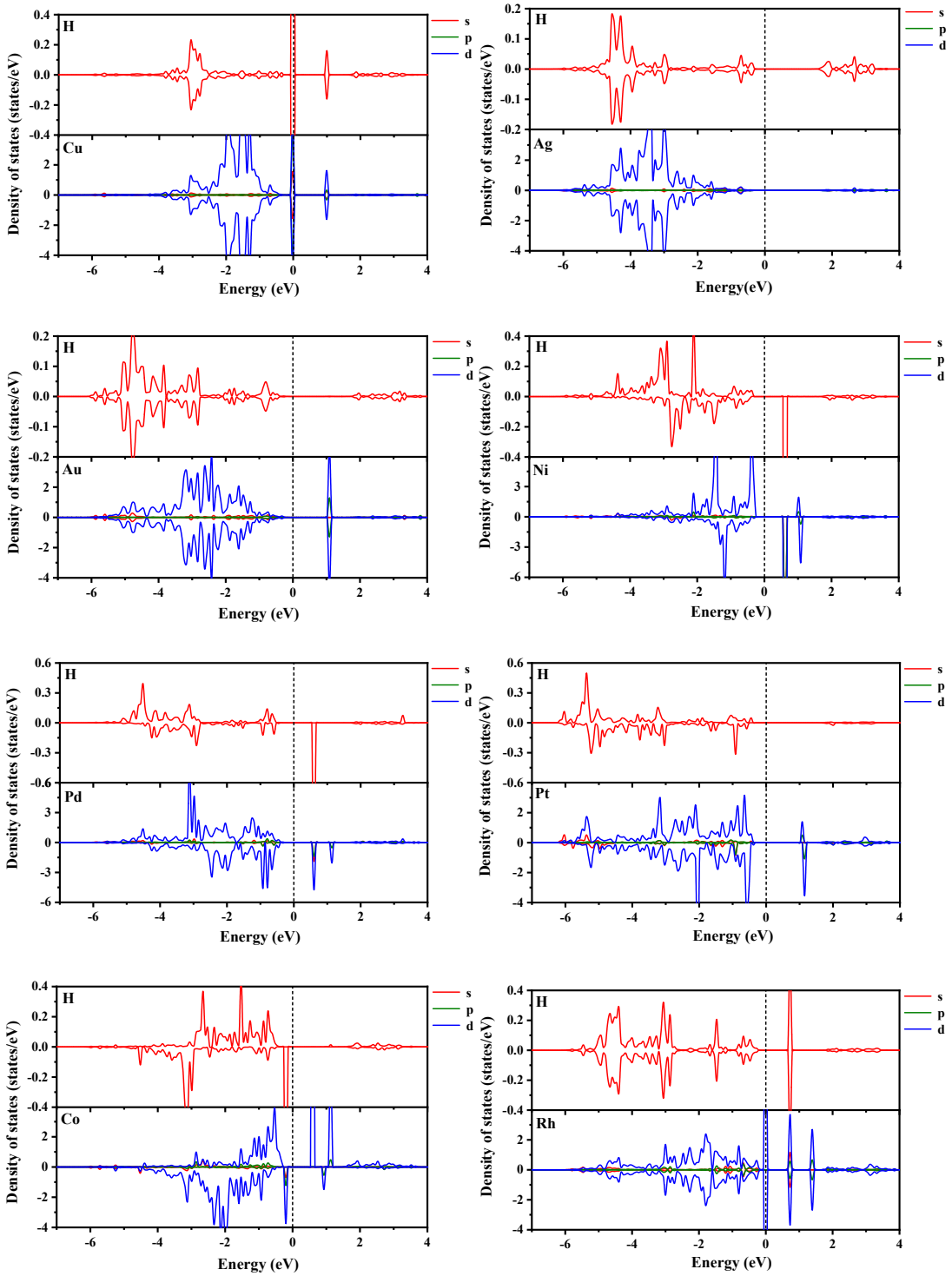


Fig. S5 A plot of the free energy of hydrogen adsorption on M-MoS_2 versus the shift of the *d*-band center.


H
Cu
Ag
Au
Ni
Pd
Pt
Co
Rh
s
p
d
Density of states (states/eV)
Energy (eV)
Energy(eV)

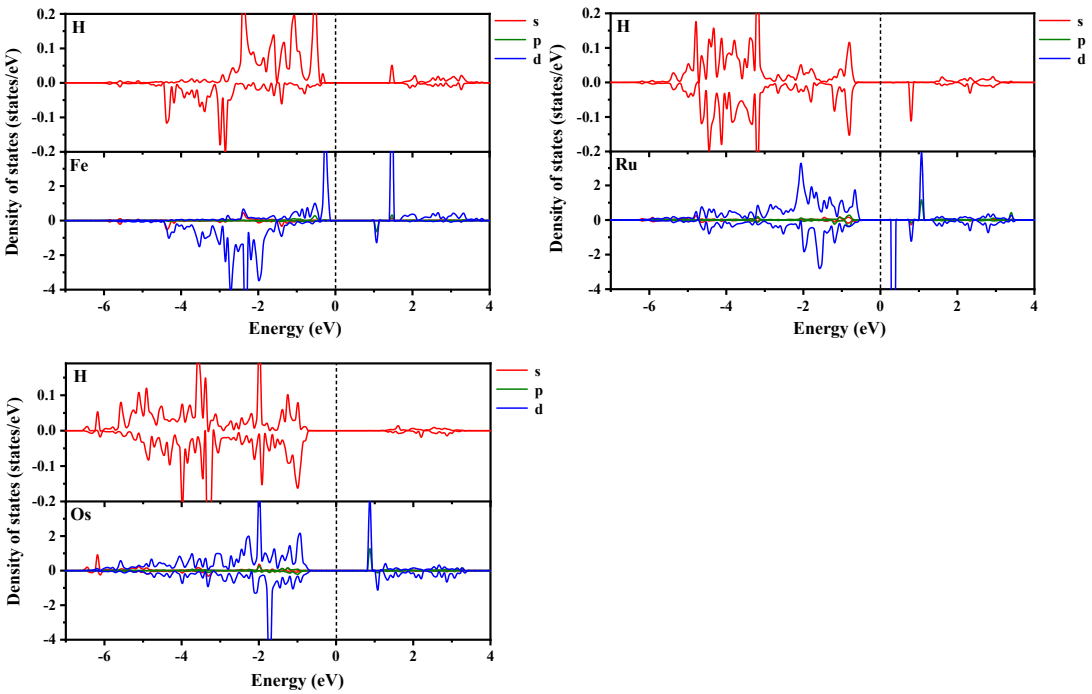


Fig. S6 Partial density of states of H adsorption on M-MoS_2.

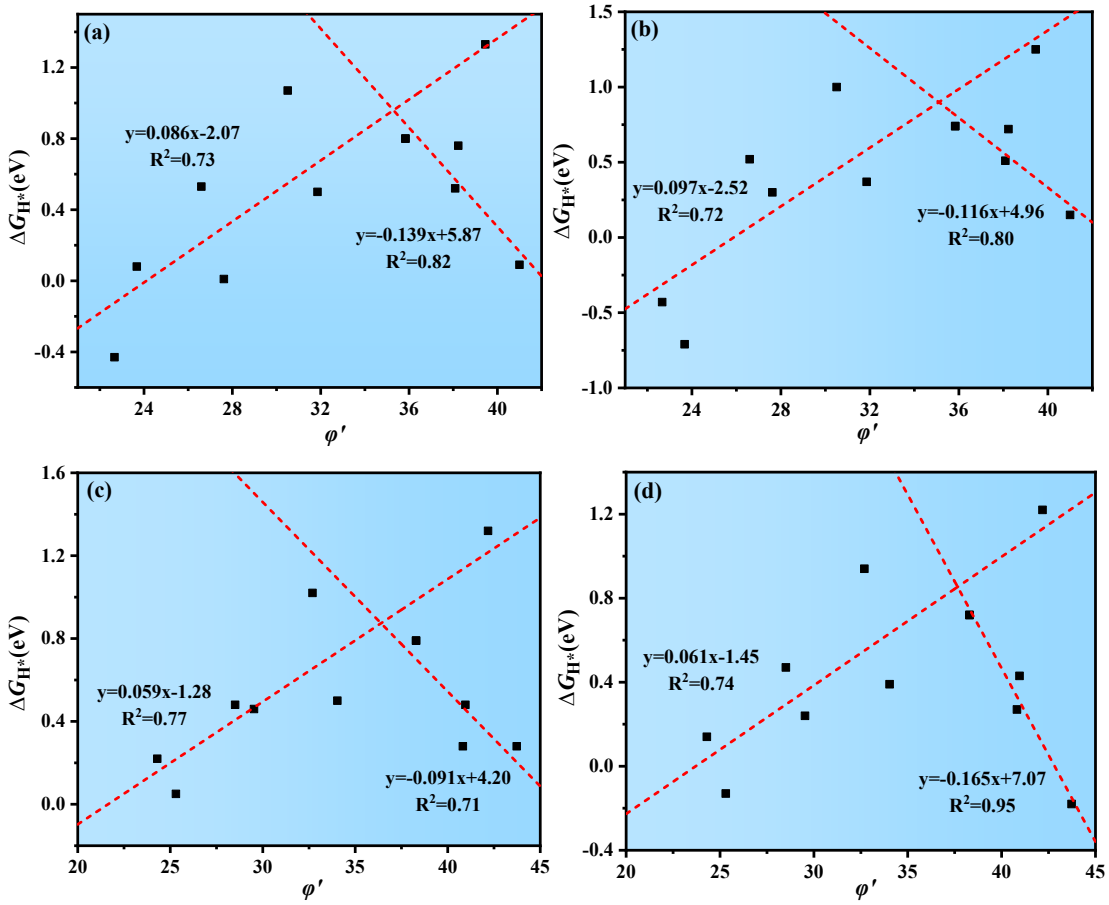


Fig. S7 Adsorption free energy of hydrogen versus the descriptor φ' for TM atoms on the substrates: (a) MoS_2; (b) $MoSe_2$; (c) WS_2; (d) WSe_2.

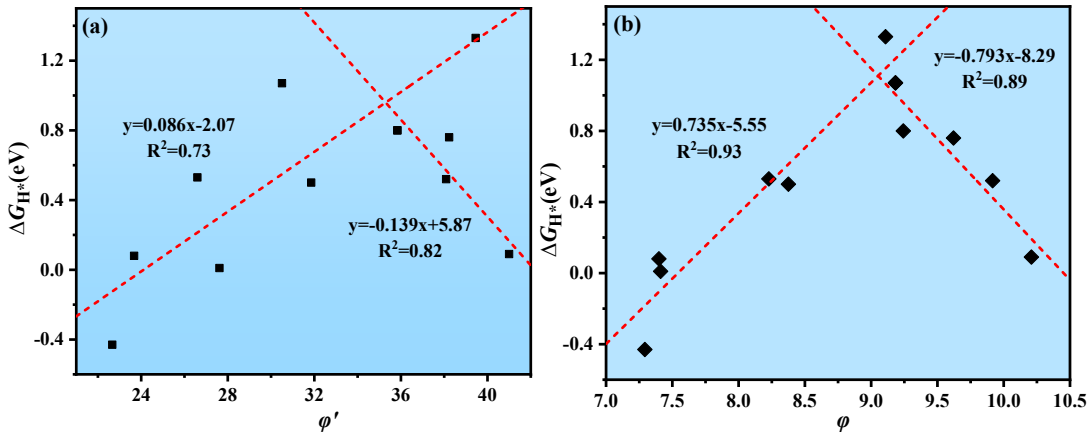
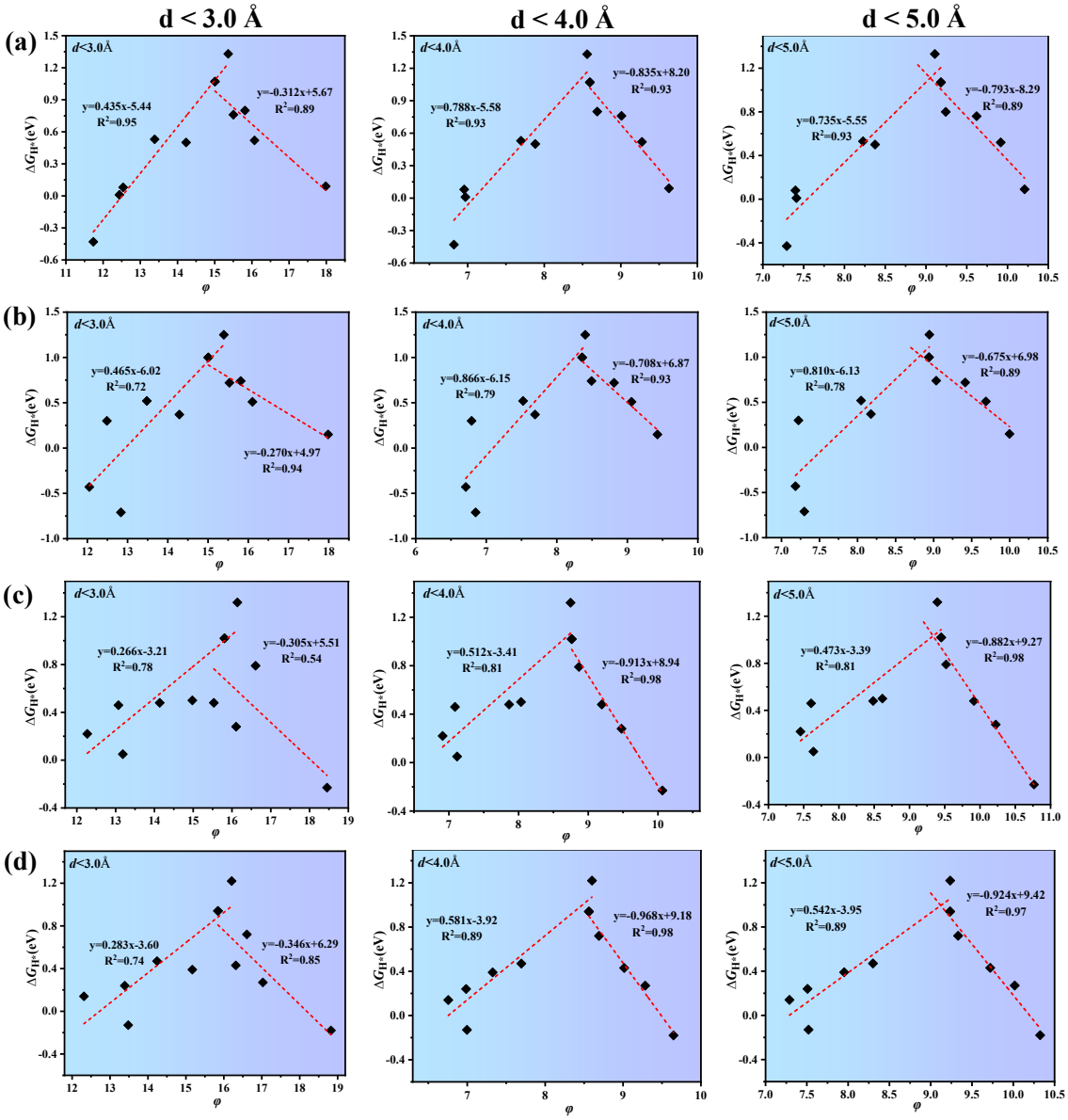


Fig. S8 Adsorption free energy of hydrogen on M-MoS_2 versus the descriptors (a) φ', (b) φ.


d < 3.0 Å
d < 4.0 Å
d < 5.0 Å
(a)
(b)
(c)
(d)
d<3.0Å
d<4.0Å
d<5.0Å
y=0.435x-5.44
R²=0.95
y=-0.312x+5.67
R²=0.89
y=0.788x-5.58
R²=0.93
y=-0.835x+8.20
R²=0.93
y=0.735x-5.55
R²=0.93
y=-0.793x-8.29
R²=0.89
y=0.465x-6.02
R²=0.72
y=-0.270x+4.97
R²=0.94
y=0.866x-6.15
R²=0.79
y=-0.708x+6.87
R²=0.93
y=0.810x-6.13
R²=0.78
y=-0.675x+6.98
R²=0.89
y=0.266x-3.21
R²=0.78
y=-0.305x+5.51
R²=0.54
y=0.512x-3.41
R²=0.81
y=-0.913x+8.94
R²=0.98
y=0.473x-3.39
R²=0.81
y=-0.882x+9.27
R²=0.98
y=0.283x-3.60
R²=0.74
y=-0.346x+6.29
R²=0.85
y=0.581x-3.92
R²=0.89
y=-0.968x+9.18
R²=0.98
y=0.542x-3.95
R²=0.89
y=-0.924x+9.42
R²=0.97
ΔG_H*(eV)
φ

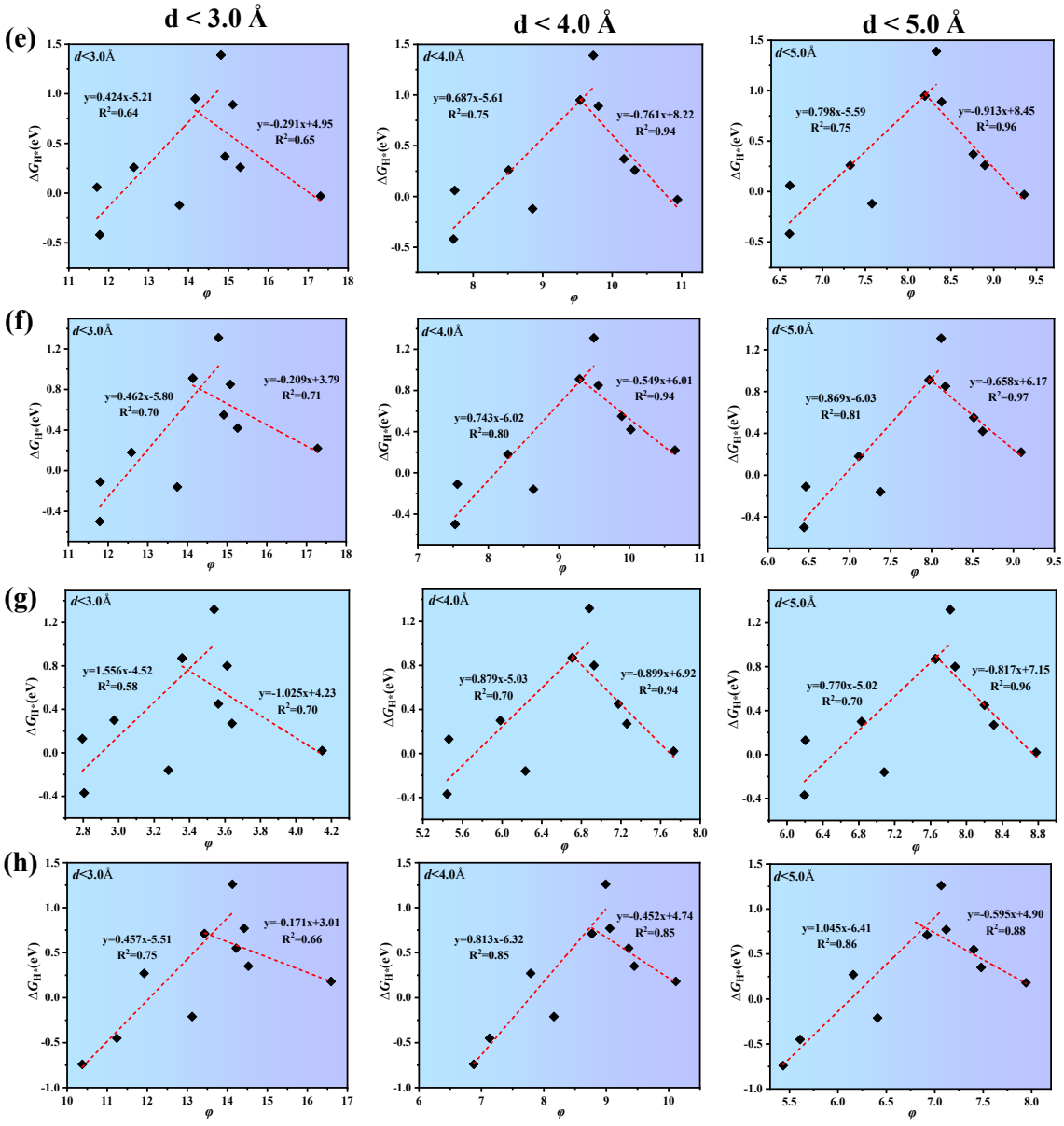
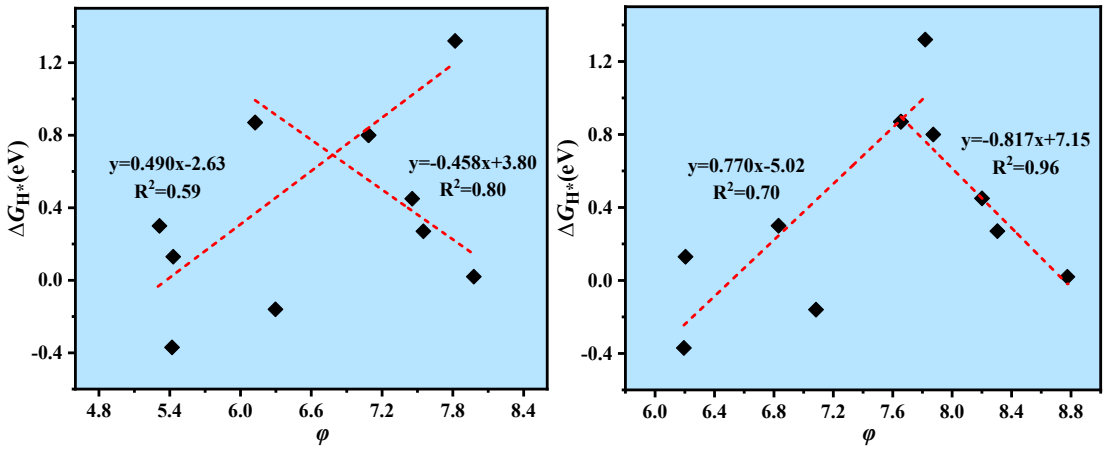
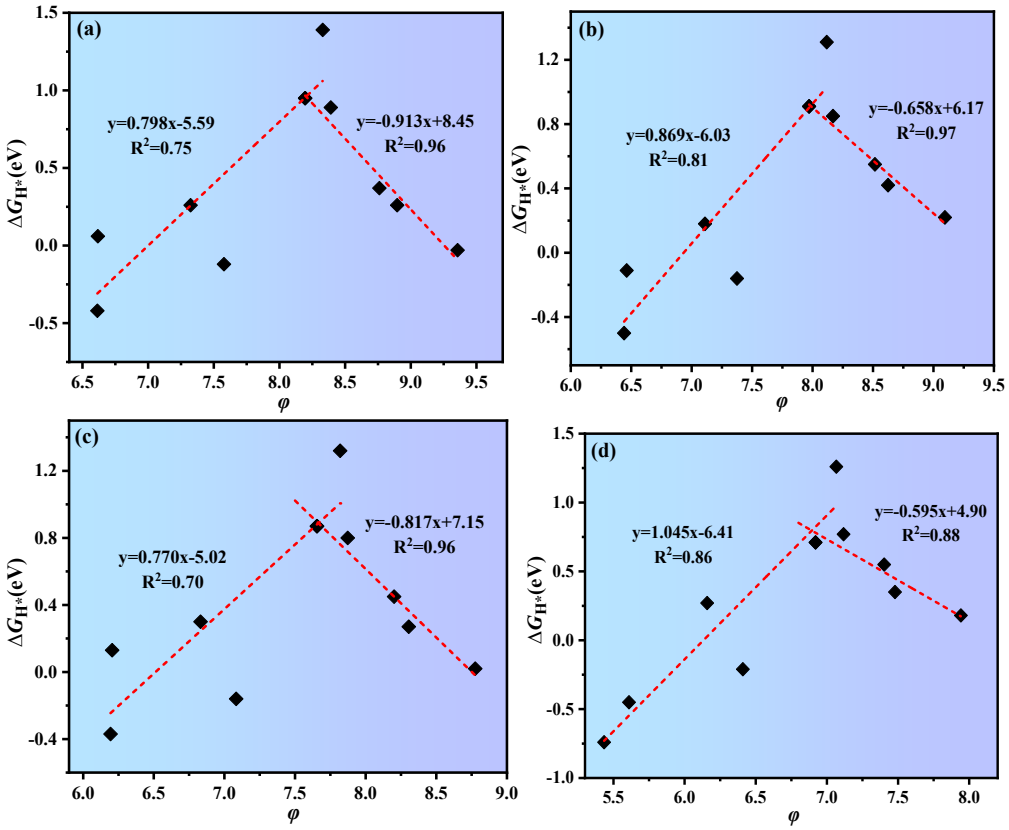


Fig. S9 Adsorption free energy of hydrogen versus the descriptor φ for TM atoms on the substrates (a) MoS_2, (b) $MoSe_2$, (c) WS_2, (d) WSe_2, (e) GaS, (f) GaSe, (g) InS and (h) InSe in different values of d.



(a) (b)

Fig. S10 Adsorption free energy of hydrogen versus the descriptor φ based on (a) $\theta_{d;}$ (b) θ_v for TM atoms on the substrate InS.



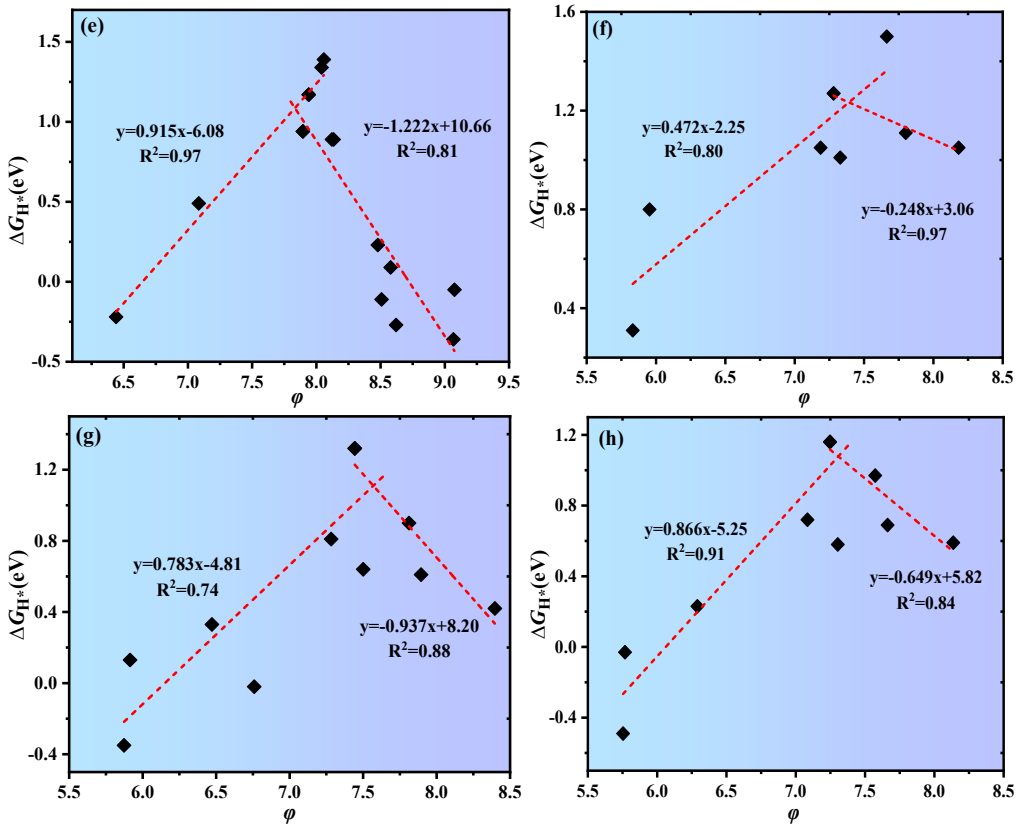


Fig. S11 Adsorption free energy of hydrogen versus the descriptor φ for TM atoms on the substrates: (a) GaS; (b) GaSe; (c) InS; (d) InSe; (e) AlX; (f) ZrS_2; (g) TlS; (h) TlSe.

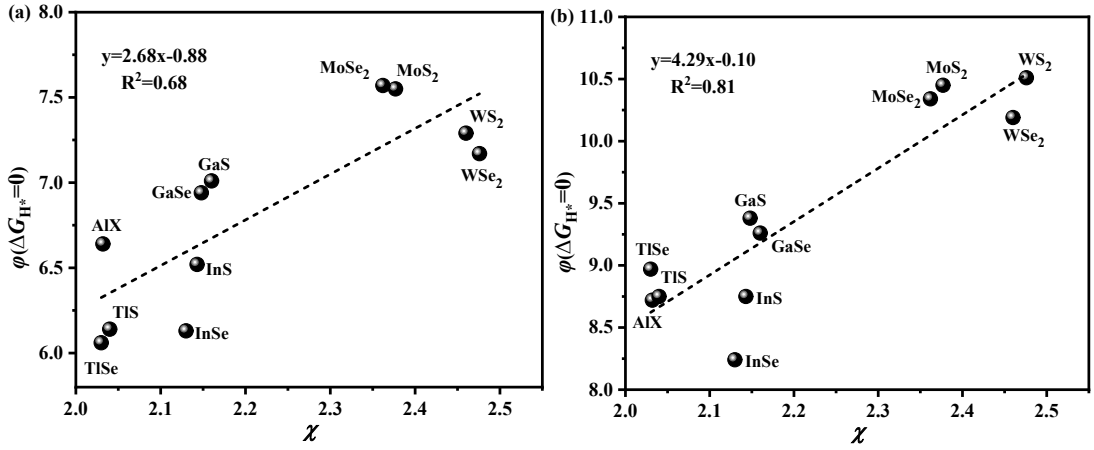


Fig. S12 The relationship between the EC and the values of φ corresponding to the adsorption free energy at 0 ($\varphi(\Delta G_{H^*}=0)$) in (a) left and (b) right of the volcanic diagram.

References

S1 J. K. Nørskov, T. Bligaard, A. Logadottir, J. R. Kitchin, J. G. Chen and S. Pandelov, *J. Electrochem. Soc.*, 2005, **152**, J23–J26.

S2 Y. A. Zhu, D. Chen, X. G. Zhou and W. K. Yuan, *Catal. Today*, 2009, **148**, 260–267.

S3 X. Lv, W. Wei, H. Wang, B. Huang and Y. Dai, *Appl. Catal. B: Environ.*, 2019, **255**, 117743.

S4 G. Gao, A. P. O'Mullane and A. Du, *ACS Catal.,* 2017, **7**, 494–500.

S5 T. He, G. Gao, L. Kou, G. Will and A. Du, *J. Catal.*, 2017, **354**, 231–235.