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## First Principles and Machine Learning Based Superior Catalytic Activities and Selectivities for N2 Reduction in MBenes, Defective 2D Materials and 2D $\pi$ -conjugated Polymer-Supported Single Atom Catalysts

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**Fig. S1.** Phonon dispersion along high symmetry directions for (a) MoB, (b) NbB, (c) TaB, and (d) TiB. As shown in the figure there is no imaginary frequency, showing the stability of structures.



Fig. S2. Views of MBene: (a) top and (b) side. The red square shows a hollow site that  $N_2$  molecules can be captured. M denotes metal. (c) Top and (d) side views of defective 2D-materials. The vacancy site of Te (Se or S) shown in red circle.



**Fig. S3.** The  $N_2$  adsorption energy and bond length enlargement for (a) TiB on metal sits, (b) TiB on hollow site, (c) HfB on metal sits, and (d) HfB on hollow site. On hollow sites both adsorption energy and N-N bond length stretching are significantly improved by nearly 2.7 times increase in the magnitude of adsorption energy and 0.15 Å increase in bond length.



**Fig. S4.** N<sub>2</sub> bond length versus adsorption energy for (a) side-on and end-on modes of 2DCPs-SACs and (b) intrinsic vacancy defect (IVD) of 2D-materials and hollow sites (HS) of MBenes.



**Fig. S5.** The  $N_2$  bond length increment versus adsorption energy for  $C_3$  graphene-based SACs with side-on and end–on adsorption modes of N-N.



Fig. S6. The  $N_2$  bond length increment versus adsorption energy for  $C_4$  graphene-based SACs with side-on and end-on adsorption modes of N-N.



Fig. S7. The  $N_2$  bond length increment versus adsorption energy for  $N_3$  graphene-based SACs with side-on and end-on adsorption modes of N-N.



**Fig. S8.** The N<sub>2</sub> bond length increment versus adsorption energy for N<sub>4</sub> graphene-based SACs with side-on and end–on adsorption modes of N-N.



Fig. S9. The  $N_2$  bond length increment versus adsorption energy for  $N_3$  (boron-nitride) graphene-based SACs with side-on and end–on adsorption modes of N-N.



Fig. S10. The  $N_2$  bond length increment versus adsorption energy for  $B_3$  (boron-nitride) graphene-based SACs with side-on and end-on adsorption modes of N-N.



Fig. S11. The  $N_2$  bond length increment versus adsorption energy for  $B_2N_2$  (boronnitride) graphene-based SACs with side-on and end–on adsorption modes of N-N.



Fig. S12. The structures which used in this study for data collection and tuning the machine learning model (a) C<sub>3</sub>, (b) C<sub>4</sub>, (c) N<sub>3</sub>, (d) N<sub>4</sub>, (e) N<sub>3</sub> (boron-nitride), (f) B<sub>3</sub> (boron-nitride), and (g) B<sub>2</sub>N<sub>2</sub> (boron-nitride) graphene-based-SACs with metal single atoms (28 transition metals) considered for screening. For each catalyst four adsorbents are considered which  $*N_2[\Delta E_{N_2}]$ ,  $*N_2H [\Delta G_{N_2-N_2H}]$ ,  $*NH_2[\Delta G_{NH_2-NH_3}]$ ,  $*NH_3[\Delta G_{NH_3-Desorbed}]$ ).



Fig. S13. PCA1 versus PCA2 for the data set.



**Fig. S14.** Diagram of free energies calculated for NRR for NbTe<sub>2</sub> without any vacancy and with Te vacancy where the red and blue curves depict free energy changes for perfect and defective NbTe<sub>2</sub>, respectively. For perfect NbTe<sub>2</sub>, free energy changes are calculated through distal mechanism. Potential determining step on vacancy site (VS) is 0.56 eV that is 1.51 eV lower than without VS.



**Fig. S15.** The pathway for  $N_2$  reduction to  $NH_3$  via dissociative-associative mechanism for NbB. As shown after the second hydrogenation step, the reduction of remaining steps is processed by attacking hydrogen to another nitrogen.



**Reaction Step** 

Fig. S16. The pathway for  $N_2$  reduction to  $NH_3$  via dissociative-associative mechanism for MnB.



**Fig. S17.** Diagram of DFT free energies for 2DCPs-SACs via enzymatic pathway at zero and applied potentials. The blue and red curves depict free energy changes for NRR at 0 and applied potentials.



**Fig. S18.** Free energies calculated for H and N<sub>2</sub> adsorption which are divided into two regions of  $\Delta G_{*H} < \Delta G_{*N2}$  (HER dominant) and  $\Delta G_{*H} > \Delta G_{*N2}$  (NRR dominant).



**Fig. S19.** Variation of energy and temperature versus time in ab initio molecular dynamic simulation for NbB. The temperature was set to 500 K (NVT ensemble with Nose-Hoover thermostat).



Fig. S20. Variation of energy and temperature versus time in ab initio molecular dynamic simulation for  $HfTe_2$  with vacancy defect. The temperature was set to 500 K (NVT ensemble with Nose-Hoover thermostat).



**Fig. S21.** Phonon dispersion along high symmetry directions for HfTe<sub>2</sub> with vacancy defect. As shown in the figure there is no imaginary frequency, showing the stability of structures.



Fig. S22. RMSE versus number of features.



**Fig. S23.** Depicting N-N bond distance, N-TM bond distance and number of hydrogen (H atoms) for (a) adsorption of  $N_2$  on the surface and (b) first hydrogenation step. Color code: TM: orange, N: blue, H: white. The shortest N-TM is considered and N-N bond distance is defined in  $N_2H_x$  (x=1,2) species.

Associative (on MS)



**Fig. S24.** Depicting of reaction steps for  $N_2$  fixation through (a) dissociative -associative and (b) associative mechanisms. (c) Charge transfer in each step of reaction with (d) free energy diagram on NbB. HS and MS refer to hollow site and Metal site, respectively.

The 2DCP (P<sup>2</sup>TANG) obtained from the molecule structure with  $D_{3h}$  symmetric tribromotrioxaazatriangulene (TBTANG).<sup>1</sup>



Fig. S25. 2DCP structure where the unit cell length is 17.1 Å.

Table S1. The defective-2D materials which used for NRR. We note that all 2D-materials are stable. The materials that are unstable or show poor catalytic activity for NRR as well as 2D structures with high formation energy, are not presented in the Table S1. The different structures are labeled as 1T, 2H, 2H<sub>a</sub> and T.



Table S2. The equation:  $E_{\text{Formation}} = E_{\text{Vacancy}} - E_{\text{total}} + \mu_X(X = Se, Te, S)$  for defect formation is applied where  $E[v_{\text{acancy}}]$  is total energy with vacancy ,  $E[_{\text{total}}]$  is total energy without vacancy and  $\mu_X$  is chemical potential of X (Se, Te, S).

System	E Formation (eV)
NbTe <sub>2</sub>	0.57
TaSe <sub>2</sub>	1.05
FeTe <sub>2</sub>	2.1
HfTe <sub>2</sub>	2.4
WTe <sub>2</sub>	2.57
MoTe <sub>2</sub>	2.6
HfSe <sub>2</sub>	2.75

Table S3. The stability energies (E) are calculated by the following equation for the 2DCPs-SACs candidates:  $E = E_{2DCPs-TM} - E_{2DCPs} - E_{TM}$ , where the  $E_{2DCPs-TM}$ ,  $E_{2DCPs}$  and  $E_{TM}$  are the energies of 2DCPs supported SACs, 2DCPs and the transition metal atom (E(M<sub>bulk</sub>)/N), respectively.

Element	Е
Sc	-2.13
Ti	-2.10
V	-0.92
Cr	-0.65
Mn	-1.59
Fe	-0.86
Со	-0.73
Ni	-0.14
Cu	0.30
Zn	-1.02
Y	-2.14
Zr	-1.78
Nb	-0.1
Мо	0.86
Tc	1.11
Ru	-0.36
Rh	-0.51
Pd	-0.42
Ag	0.88
Cd	0.06
Hf	-1.58
Та	0.28
W	1.41
Re	1.26
Os	0.87
Ir	-0.02
Pt	-0.17
Au	0.65

Elementary Steps	ΔG	$\Delta G_{sol}$
$*N-*N+(H^++e^-) \rightarrow *NH-*N$	-0.08	-0.04
*NH-*N + (H <sup>+</sup> +e <sup>-</sup> ) $\rightarrow$ *NH <sub>2</sub> -*N	-1.06	-1.17
$*NH_2-*N + (H^++e^-) \rightarrow *N + NH_3(g)$	+0.06	+0.01
$*N + (H^+ + e^-) \rightarrow *NH$	+0.25	+0.12
*NH + (H <sup>+</sup> +e <sup>-</sup> ) $\rightarrow$ *NH <sub>2</sub>	-0.05	-0.22
$*NH_2 + (H^+ + e^-) \rightarrow *NH_3$	+0.40	+0.30

Table S4. Free energy charges for NbB without and with considering the solvation effect.

Table S5. Comparison of adsorption free energy changes of N<sub>2</sub> and H<sub>2</sub>O on the selected catalysts.

	TaB	NbTe <sub>2</sub>	NbB	HfTe <sub>2</sub>	MoB	MnB	HfSe <sub>2</sub>	TaSe <sub>2</sub>	Nb@ SAC
$\Delta G_{N2}^{*}(eV)$	-1.96	-1.25	-1.52	-2.55	-1.01	-0.30	-1.07	-0.27	-0.59
$\Delta G^*_{H2O}(eV)$	-0.81	-0.59	-0.75	-0.71	-0.10	-0.10	-0.95	-0.40	-0.55

Hyperparameter	Value
Learning rate	0.049
Max_depth	8
Random_state	42
Min_child_weight	10
N_estimators	300
Num_leaves	31

Table S6. The most important hyperparameter which used by LGBM regression model.

We obtained the experimental value of the overall free energy of NRR in solution by considering the solvation effect. In standard condition of 1 M N<sub>2</sub>, H<sub>2</sub>, and NH<sub>3</sub> in aqueous solution, the  $\Delta G^{\circ}$  value is estimated to be -1.2 eV.

 $\begin{array}{ll} N_2(g) + 3H_2(g) \rightarrow 2NH_3(g) & \Delta G^\circ = -3.94 \times 2 \ \text{kcal/mol} = 7.88 \ \text{kcal/mol} = -0.34 \ \text{eV} \ (g) \\ N_2(aq) + 3H_2(aq) \rightarrow 2NH_3(aq) & \Delta G^\circ = -6.35 \times 2 - 4.2 \times 3 - 2.5 \times 1 = -27.8 \ \text{kcal/mol} = -1.2 \ \text{eV} \ (aq) \\ (aq \ \text{denotes the standard condition in 1 M in aqueous solution}). \end{array}$ 

Compound	Solvation Free energy (eV)	Reference
N <sub>2</sub> (aq)	0.1 (2.5 kcal/mol)	2
H <sub>2</sub> (aq, standard 1 M)	0.18 (+4.2 kcal/mol)	3
NH <sub>3</sub> (aq, standard 1M)	-0.28 (-6.35 kcal/mol)	3

Table S7. Solvation free energy of some compounds.

 Table S8. Free energy of formation for some compounds.

Compound	Formation Free energy (eV)	Reference
N <sub>2</sub> (g)	0	3
H <sub>2</sub> (g)	0	3
NH <sub>3</sub> (g)	-0.17 (-3.94 kcal/mol)	3

## Supplementary note1:

The overpotential can be computed as follows:

 $\eta {=} U_{equilibrium} {-} U_{limiting}$ 

where  $U_{equilibrium}$  is the equilibrium potential for NRR (-0.16 V for the reaction  $N_2+6H^++6e^- \rightarrow 2NH_3$ ) and  $U_{limiting}$  is the lowest negative potential which is calculated with the following equation:  $U_{limiting} = -\Delta G_{max}/e$ .

## References

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