

## Supporting Information for:

# A Simple Descriptor for Nitrogen Reduction Reaction over Single Atom Catalysts

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### 1. Calculation method of NRR activity

The change in free energy is calculated by the following formula:<sup>1</sup>

$$\Delta G = \Delta E + \Delta E_{ZPE} - T\Delta S + \Delta G_U + \Delta G_{pH} \quad (1)$$

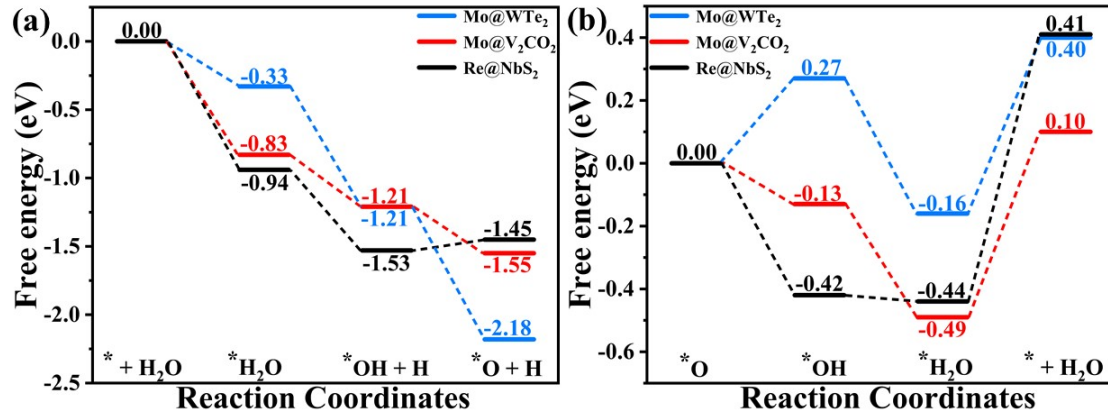
Where  $\Delta E$  refers to the energy obtained by DFT calculation,  $\Delta G_U = -eU$ , where  $U$  is the electrode potential,  $e$  is the number of transferred electrons;  $\Delta G_{pH} = k_B T \ln 10 \times pH$ , in this work,  $pH = 0$  was employed.  $\Delta E_{ZPE}$  is the difference between the zero point energy (ZPE) of adsorbed intermediates and gas phase intermediates,  $T$  is the temperature (298.15 K), and  $\Delta S$  is the change of entropy between the adsorption state and the gas phase. The entropy of the gas phase molecule is obtained by the NIST database, and the entropy and zero-point energy of the adsorbate can be obtained by calculating the vibration frequency where the entropy value is calculated by:<sup>2</sup>

$$S(T) = \sum_{i=1}^{3N} \left[ -R \ln \left( 1 - e^{-\frac{hv_i}{k_B T}} \right) + \frac{N_A hv_i}{T} \frac{e^{-hv_i/k_B T}}{1 - e^{-hv_i/k_B T}} \right] \quad (2)$$

Where  $R$  stands for the ideal gas constant,  $k_B$  is Boltzmann constant,  $h$  is Planck constant,  $N_A$  is Avogadro constant,  $v_i$  represents the vibration of the normal mode, and  $N$  represents the number of adsorbed atoms. And the calculated ZPE and TS of different NRR intermediates were given in Table S4.

It should be noted that SACs can be oxidized easily, due to the high reactivity of the supported metal atoms. Taking  $\text{Mo@WTe}_2$ ,  $\text{Mo@V}_2\text{CO}_2$  and  $\text{Re@NbS}_2$  as examples, our results show that the adsorption and dissociation of  $\text{H}_2\text{O}$  are all exothermic, making

the \*O or \*OH adsorbed metal sites are thermodynamically more favorable than the pristine metal sites at  $U = 0$  V (Figure S1a). However, under the reaction condition of NRR, the adsorbed \*O or \*OH species can be reduced. To prove this point, a constant-potential method (cpm) was used to calculate the free energy diagram for the reduction of metal sites under the reaction condition ( $U = -0.5$  V was considered herein), as referred to previous work.<sup>3-5</sup> Our results show that the adsorbed \*O or \*OH species can be reduced to \*H<sub>2</sub>O (Figure S1b) rapidly. Based on this consideration, \*O or \*OH adsorbed SACs were not considered in our work.



**Figure S1.** Free energy diagram for the (a) oxidation process (at  $U = 0$  V) and (b) reduction process ( $U = -0.5$  V vs RHE) of the single metal atom in Mo@WTe<sub>2</sub>, Mo@V<sub>2</sub>CO<sub>2</sub> and Re@NbS<sub>2</sub>, respectively.

## 2. Calculation method of TM binding energy.

The binding energy ( $E_b$ ) of the TM is calculated by:<sup>6</sup>

$$E_b = E_{TM-sub} - E_{sub} - E_{TM} \quad (3)$$

Where  $E_{TM-sub}$ ,  $E_{sub}$ , and  $E_{TM}$  represent the total energy of the TM loaded substrate, the energy of the substrate, and the energy of the isolated TM, respectively. According to the definition of binding energy, the smaller the value of binding energy, the stronger the TM bond with the substrate.

## 3. Calculation method of the electronegativity of the substrate

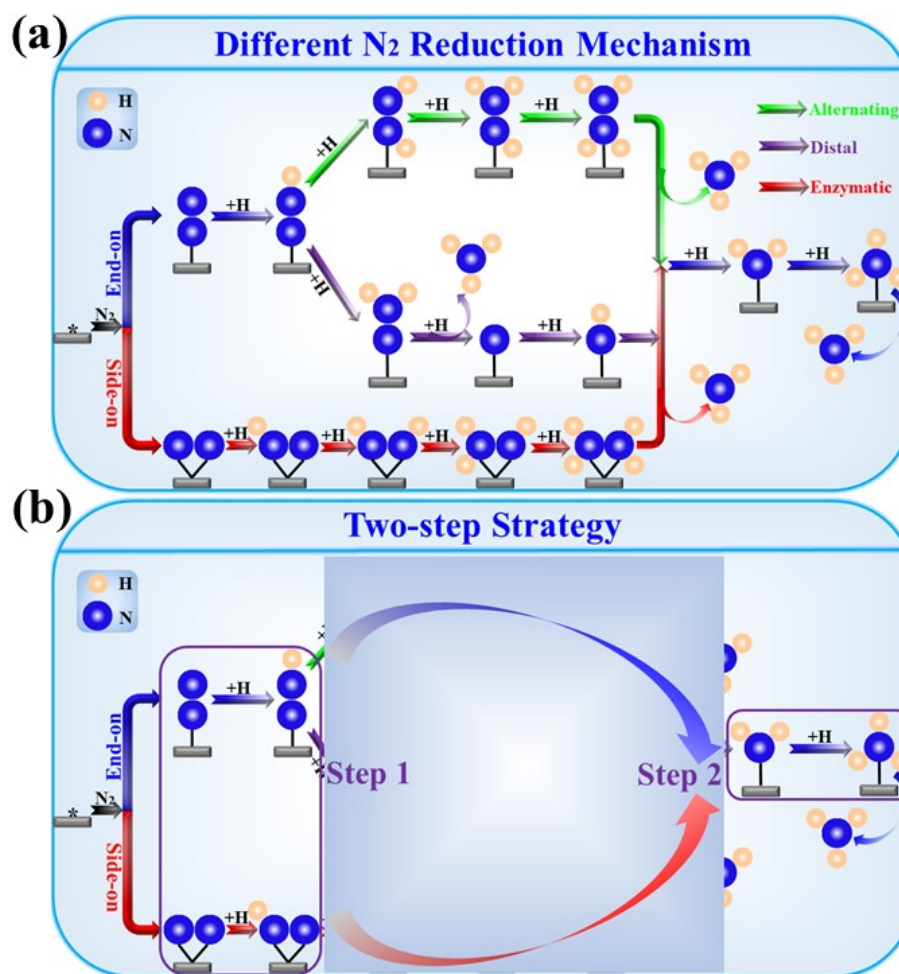
The electronegativity of the substrate ( $\chi_{sub}$ ) is calculated by:

$$\chi_{sub} = \frac{\sum n_i \chi_i}{\sum n_i} \quad (4)$$

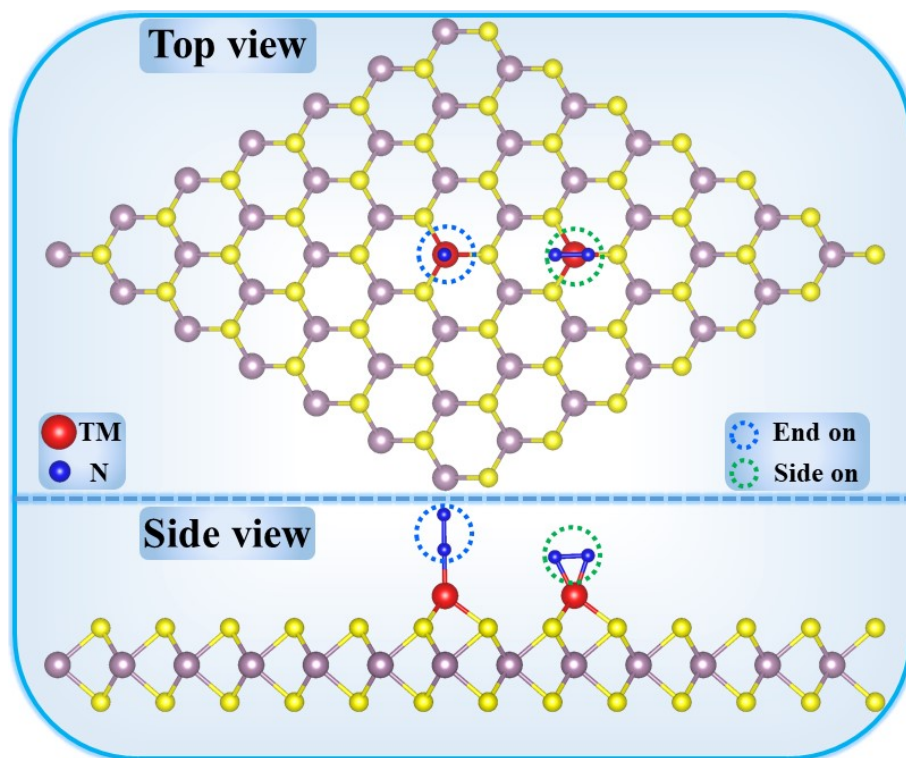
where  $n_i$  and  $\chi_i$  are the number and electronegativity of  $i$ 'th element, respectively. And the calculated  $\chi_{\text{sub}}$  of different substrates were given in Table S2.

#### 4. Figures and Tables

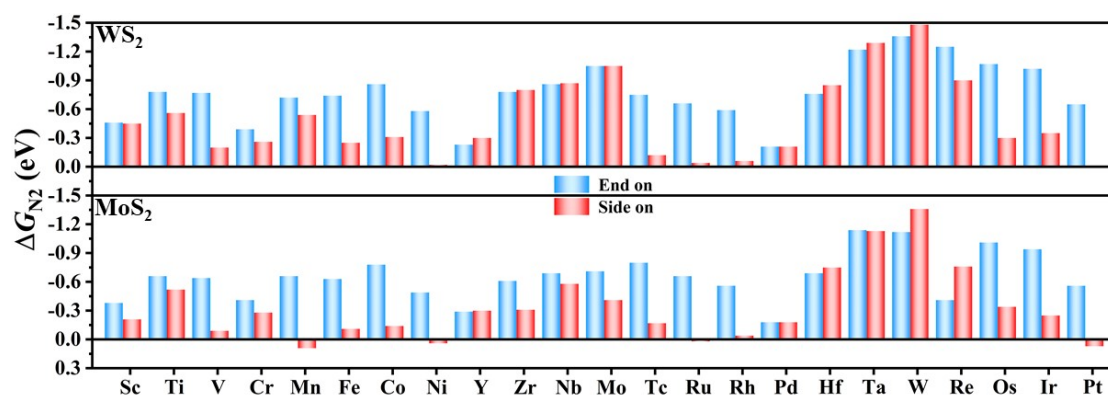
Figures:



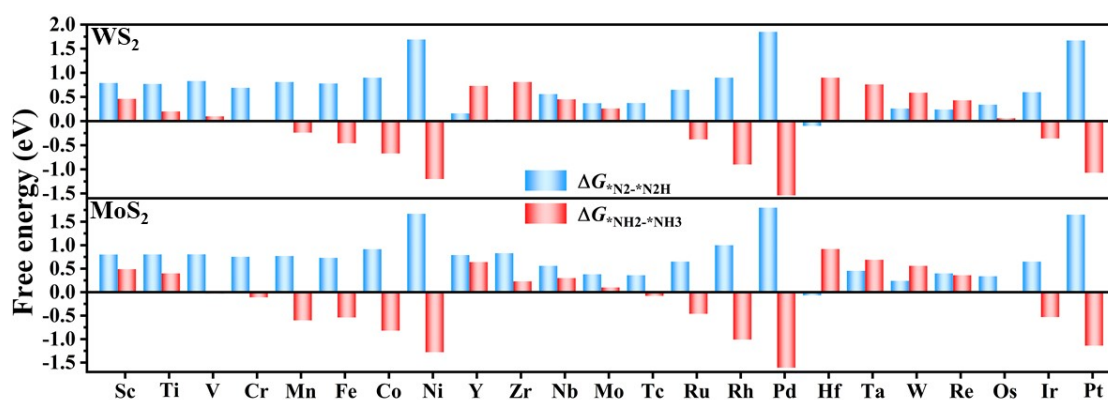
**Figure S2.** (a) Different reaction mechanisms of NRR, where green, purple, and red pathway stand for alternating, distal, and enzymatic mechanisms, respectively. (b) Flowchart of the two-step screening procedure for NRR catalysts.



**Figure S3.** Top view and Side view of the different N<sub>2</sub> adsorption configuration on the catalytic site, where the end on and side on adsorption pattern are marked by the blue and green dotted circle, respectively.



**Figure S4.** Calculated  $N_2$  adsorption free energy ( $\Delta G^*_{N_2}$ ) of various TM@Mo/WS<sub>2</sub> with end on and side on adsorption patterns.



**Figure S5.** Calculated free energy change of the first ( $\Delta G^*_{N_2 \rightarrow N_2H}$ ) and last ( $\Delta G^*_{NH_2 \rightarrow NH_3}$ ) hydrogenation steps of different TM@MX<sub>2</sub>. (a) TM@MoS<sub>2</sub>, (b) TM@WS<sub>2</sub>.

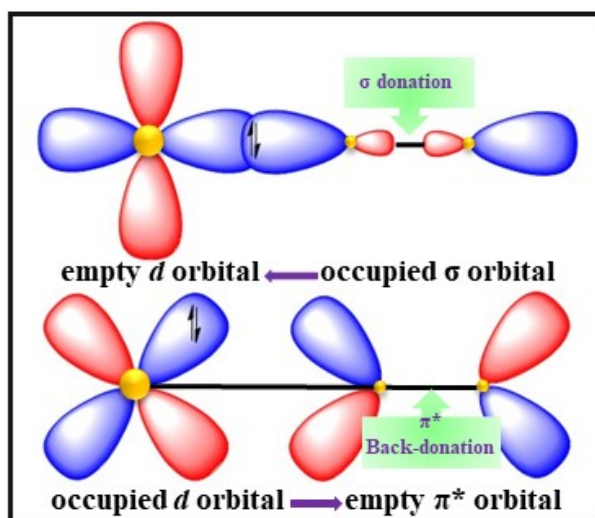


Figure S6. Simplified schematic diagram of  $N_2$  bonding to single TM atom.

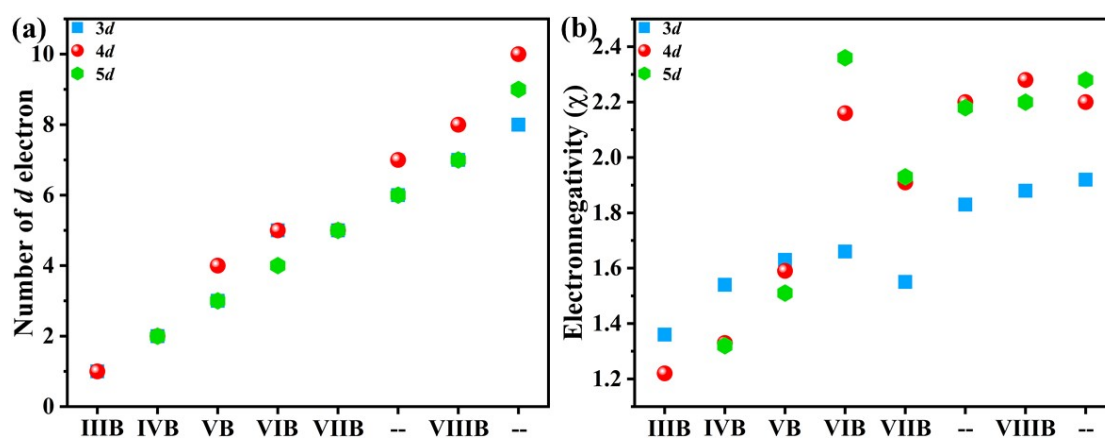
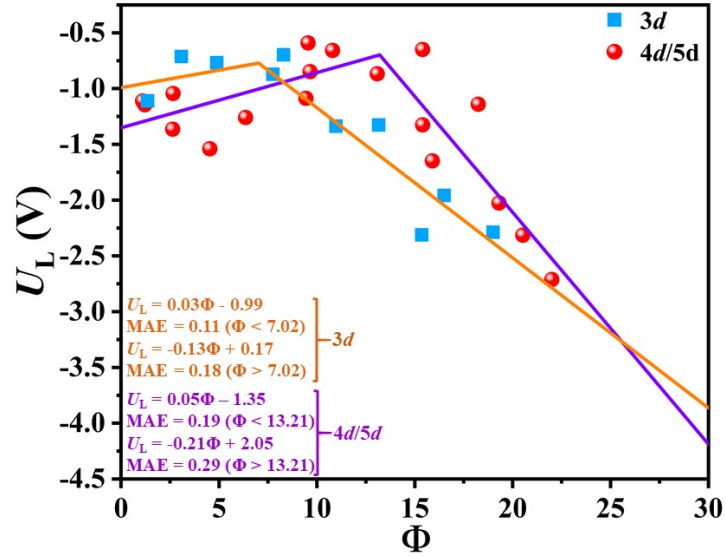
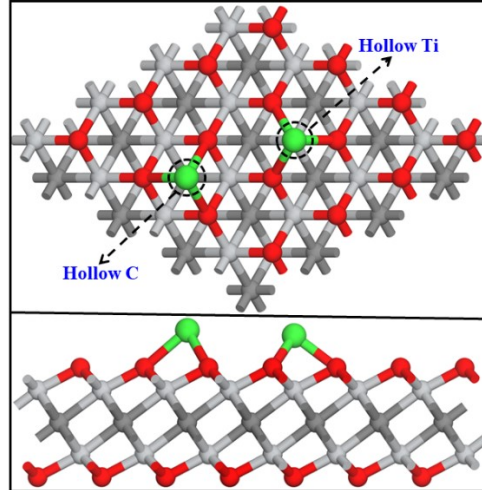


Figure S7. (a) Number of  $d$  electrons and (b) the electronegativity of  $3d$ ,  $4d$  and  $5d$  TM atoms.

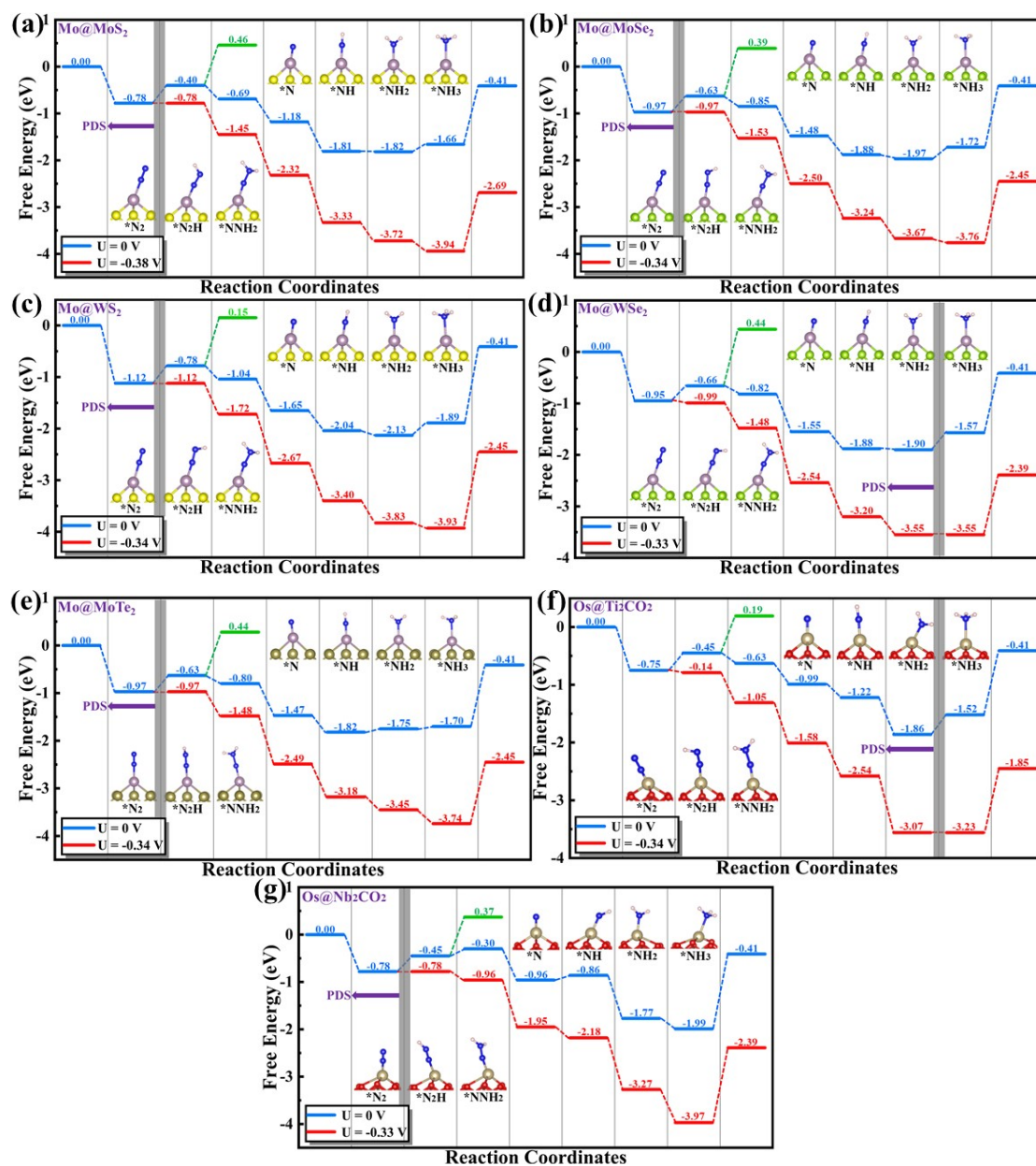


**Figure S8.** Fitted volcano diagram between the  $U_L$  and the descriptor  $\Phi$  of TM-N<sub>4</sub>, insets are the fitted functions and MAE of the 3d and 4d/5d TM, respectively.



**Figure S9.** Top view and side view binding configuration of the TM atoms anchored on Ti<sub>2</sub>CO<sub>2</sub> substrates, where red, green, light gray and dark gray balls represent O, TM, Ti and C atoms, respectively.





**Figure S10.** Calculated free energy diagram of the optimal NRR reaction pathway of different catalysts at the potential of 0 V (blue pathway) and the corresponding limiting potential ( $U_L$ ) (red pathway), respectively, and insets are the coordination configurations of different intermediates. (a)  $Mo@MoS_2$ , (b)  $Mo@MoSe_2$ , (c)  $Mo@WS_2$ , (d)  $Mo@WSe_2$ , (e)  $Mo@MoTe_2$ , (f)  $Os@Ti_2CO_2$ , (g)  $Os@Nb_2CO_2$ .

**Tables:**

**Table S1. The specific values of different features**

Elements	$N_d$	Electronegativity ( $\chi$ )	Elements	$N_d$	Electronegativity ( $\chi$ )
Sc	1	1.36	Rh	8	2.28
Ti	2	1.54	Pd	10	2.20
V	3	1.63	Hf	2	1.32
Cr	5	1.66	Ta	3	1.51
Mn	5	1.55	W	4	2.36
Fe	6	1.83	Re	5	1.93
Co	7	1.88	Os	6	2.18
Ni	8	1.92	Ir	7	2.20
Y	1	1.22	Pt	9	2.28
Zr	2	1.33	O		3.44
Nb	4	1.59	S		2.58
Mo	5	2.16	Se		2.55
Tc	5	1.91	Te		2.12
Ru	7	2.20	C		2.55

**Table S2. Calculated electronegativity of different substrates ( $\chi_{sub}$ ) and the number of electrons of Mo single atom transferred to the different substrates.**

Catalysts	$\chi_{sub}$	Electron number (e <sup>-</sup> )	Catalysts	$\chi_{sub}$	Electron number (e <sup>-</sup> )
Mo@MoS <sub>2</sub>	2.440	0.82	Mo@WTe <sub>2</sub>	2.200	0.26
Mo@MoSe <sub>2</sub>	2.420	0.49	Mo@NbS <sub>2</sub>	2.250	1.04
Mo@WS <sub>2</sub>	2.507	0.60	Mo@Ti <sub>2</sub> CO <sub>2</sub>	2.502	1.26
Mo@WSe <sub>2</sub>	2.487	0.40	Mo@V <sub>2</sub> CO <sub>2</sub>	2.538	1.46
Mo@MoTe <sub>2</sub>	2.133	0.32	Mo@Nb <sub>2</sub> CO <sub>2</sub>	2.522	1.15

Table S3. Calculated and predicted NRR performance of the most promising two TM supported on different substrates, and the corresponding error and mean absolute error (MAE).

Properties	MoSe <sub>2</sub>		WSe <sub>2</sub>		MoTe <sub>2</sub>	
Elements	Mo	Os	Mo	Os	Mo	Re
$\Phi$	4.46	5.40	4.34	5.26	5.06	4.52
Prediction (V)	-0.35	-0.32	-0.37	-0.26	-0.27	-0.34
Calculation (V)	-0.34	-0.34	-0.33	-0.35	-0.34	-0.39
Error (V)	-0.01	0.02	-0.04	0.09	0.07	0.05
Properties	WTe <sub>2</sub>		NbS <sub>2</sub>		Ti <sub>2</sub> CO <sub>2</sub>	
Elements	Mo	Re	Mo	Re	Mo	Os
$\Phi$	4.91	4.39	4.80	4.29	4.32	5.23
Prediction (V)	-0.29	-0.36	-0.31	-0.37	-0.37	-0.25
Calculation (V)	-0.32	-0.46	-0.41	-0.31	-0.41	-0.34
Error (V)	0.03	0.10	0.10	-0.06	0.04	0.09
Properties	V <sub>2</sub> CO <sub>2</sub>		Nb <sub>2</sub> CO <sub>2</sub>			
Elements	Mo	Os	Mo	Os		
$\Phi$	4.26	5.15	4.28	5.19		
Prediction (V)	-0.38	-0.26	-0.37	-0.26		
Calculation (V)	-0.24	-0.36	-0.40	-0.33		
Error (V)	-0.14	0.10	0.03	0.07		
MAE (V)			0.065			

Table S4. Calculated zero point energies and entropy of different adsorption species, where the \* denotes the adsorption site.-

	Adsorption Species	E <sub>ZPE</sub> (eV)	-TS (eV)
Side on	*N≡*N	0.18	-0.19
	*N=*NH	0.47	-0.18
End on	*N≡N	0.20	-0.19
	*N=*NH	0.46	-0.21
Alternating pathway	*NH-NH	0.85	-0.10
	*NH-NH <sub>2</sub>	1.15	-0.18
	*NH <sub>2</sub> -NH <sub>2</sub>	1.44	-0.19
Distal pathway	*N-NH <sub>2</sub>	0.84	-0.15
	*N	0.08	-0.06
	*NH	0.35	-0.09
	*NH <sub>2</sub>	0.65	-0.15
	*NH <sub>3</sub>	1.02	-0.19

**Table S5.** Calculated binding energy of the TM anchored on two different sites on the MXenes supports.

Catalysts	$E_b$ -Hollow C (eV)	$E_b$ -Hollow TM (eV)
Os@Ti <sub>2</sub> CO <sub>2</sub>	-3.38	-1.98
Mo@V <sub>2</sub> CO <sub>2</sub>	-5.15	-4.85
Os@Nb <sub>2</sub> CO <sub>2</sub>	-2.94	-2.00

**Table S6.** Calculated hydrogenation free energy changes of different intermediates through Alternating (green) and Distal (purple) pathway on Mo@MoS<sub>2</sub> and Mo@MoSe<sub>2</sub>.

Catalyst	Species	$\Delta G$ (eV)	Catalyst	Species	$\Delta G$ (eV)
Mo@MoS <sub>2</sub>	*	0	Mo@MoSe <sub>2</sub>	*	0
	*N <sub>2</sub>	-0.78		*N <sub>2</sub>	-0.97
	*N <sub>2</sub> H	0.38		*N <sub>2</sub> H	0.34
	*NHNH	0.86		*NHNH	1.02
	*NHNH <sub>2</sub>	-0.71		*NHNH <sub>2</sub>	-0.75
	*NH <sub>2</sub> NH <sub>2</sub>	0.40		*NH <sub>2</sub> NH <sub>2</sub>	0.41
	*NNH <sub>2</sub>	-0.29		*NNH <sub>2</sub>	-0.22
	*N	-0.49		*N	-0.63
	*NH	-0.63		*NH	-0.40
	*NH <sub>2</sub>	-0.01		*NH <sub>2</sub>	-0.09
	*NH <sub>3</sub>	0.16		*NH <sub>3</sub>	0.25
	* + NH <sub>3</sub>	1.26		* + NH <sub>3</sub>	1.31

**Table S7. Calculated hydrogenation free energy changes of different intermediates through Alternating (green) and Distal (purple) pathway on Mo@WS<sub>2</sub> and Mo@WSe<sub>2</sub>.**

Catalyst	Species	$\Delta G$ (eV)	Catalyst	Species	$\Delta G$ (eV)
Mo@WS <sub>2</sub>	*	0	Mo@WSe <sub>2</sub>	*	0
	*N <sub>2</sub>	-1.12		*N <sub>2</sub>	-0.95
	*N <sub>2</sub> H	0.34		*N <sub>2</sub> H	0.29
	*NHNH	0.93		*NHNH	1.10
	*NHNH <sub>2</sub>	-0.70		*NHNH <sub>2</sub>	-0.67
	*NH <sub>2</sub> NH <sub>2</sub>	0.41		*NH <sub>2</sub> NH <sub>2</sub>	0.41
	*NNH <sub>2</sub>	-0.26		*NNH <sub>2</sub>	-0.16
	*N	-0.61		*N	-0.73
	*NH	-0.39		*NH	-0.33
	*NH <sub>2</sub>	-0.09		*NH <sub>2</sub>	-0.02
	*NH <sub>3</sub>	0.24		*NH <sub>3</sub>	0.33
	* + NH <sub>3</sub>	1.47		* + NH <sub>3</sub>	1.16

**Table S8. Calculated hydrogenation free energy changes of different intermediates through Alternating (green) and Distal (purple) pathway on Mo@MoTe<sub>2</sub> and Mo@WTe<sub>2</sub>.**

Catalyst	Species	$\Delta G$ (eV)	Catalyst	Species	$\Delta G$ (eV)
Mo@MoTe <sub>2</sub>	*	0	Mo@WTe <sub>2</sub>	*	0
	*N <sub>2</sub>	-0.97		*N <sub>2</sub>	-0.98
	*N <sub>2</sub> H	0.34		*N <sub>2</sub> H	0.32
	*NHNH	0.91		*NHNH	0.95
	*NHNH <sub>2</sub>	-0.59		*NHNH <sub>2</sub>	-0.60
	*NH <sub>2</sub> NH <sub>2</sub>	0.35		*NH <sub>2</sub> NH <sub>2</sub>	0.41
	*NNH <sub>2</sub>	-0.17		*NNH <sub>2</sub>	-0.17
	*N	-0.67		*N	-0.76
	*NH	-0.35		*NH	-0.28
	*NH <sub>2</sub>	0.07		*NH <sub>2</sub>	-0.02
	*NH <sub>3</sub>	0.05		*NH <sub>3</sub>	0.26
	* + NH <sub>3</sub>	1.29		* + NH <sub>3</sub>	1.22

**Table S9. Calculated hydrogenation free energy changes of different intermediates through Alternating (green) and Distal (purple) pathway on Mo@NbS<sub>2</sub> and Os@Ti<sub>2</sub>CO<sub>2</sub>.**

Catalyst	Species	$\Delta G$ (eV)	Catalyst	Species	$\Delta G$ (eV)
Re@NbS <sub>2</sub>	*	0	Os@Ti <sub>2</sub> CO <sub>2</sub>	*	0
	*N <sub>2</sub>	-1.00		*N <sub>2</sub>	-0.75
	*N <sub>2</sub> H	0.25		*N <sub>2</sub> H	0.30
	*NHNH	0.83		*NHNH	0.64
	*NHNH <sub>2</sub>	-1.26		*NHNH <sub>2</sub>	-0.76
	*NH <sub>2</sub> NH <sub>2</sub>	0.70		*NH <sub>2</sub> NH <sub>2</sub>	-0.20
	*NNH <sub>2</sub>	-0.40		*NNH <sub>2</sub>	-0.18
	*N	0.31		*N	-0.36
	*NH	-0.95		*NH	-0.23
	*NH <sub>2</sub>	-0.49		*NH <sub>2</sub>	-0.64
	*NH <sub>3</sub>	0.10		*NH <sub>3</sub>	0.34
* + NH <sub>3</sub>	1.75	* + NH <sub>3</sub>	1.09		

**Table S10. Calculated hydrogenation free energy changes of different intermediates through Alternating (green) and Distal (purple) pathway on Mo@V<sub>2</sub>CO<sub>2</sub> and Os@Nb<sub>2</sub>CO<sub>2</sub>.**

Catalyst	Species	$\Delta G$ (eV)	Catalyst	Species	$\Delta G$ (eV)
Mo@V <sub>2</sub> CO <sub>2</sub>	*	0	Os@Nb <sub>2</sub> CO <sub>2</sub>	*	0
	*N <sub>2</sub>	-0.14		*N <sub>2</sub>	-0.78
	*N <sub>2</sub> H	0.24		*N <sub>2</sub> H	0.33
	*NHNH	0.56		*NHNH	0.82
	*NHNH <sub>2</sub>	-1.47		*NHNH <sub>2</sub>	-0.86
	*NH <sub>2</sub> NH <sub>2</sub>	0.43		*NH <sub>2</sub> NH <sub>2</sub>	-0.10
	*NNH <sub>2</sub>	-0.67		*NNH <sub>2</sub>	0.15
	*N	-0.29		*N	-0.66
	*NH	-0.72		*NH	0.10
	*NH <sub>2</sub>	-0.29		*NH <sub>2</sub>	-0.91
	*NH <sub>3</sub>	0.08		*NH <sub>3</sub>	-0.22
* + NH <sub>3</sub>	1.37	* + NH <sub>3</sub>	1.57		

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