Supplementary Materials

N-heterocyclic carbene coordinated single atom catalysts on C_2N for enhanced nitrogen reduction

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Computational methods

The binding energy (E_b) is defined as:

$$E_b = E_{TM@C_2N-NCM} - E_{TM} - E_{C_2N-NCM} \tag{1}$$

in which $E_{TM@C_2N-NCM}$ represents the total energy of C_2N-NCM after absorbing TM, E_{TM} denotes the energy of the isolated single transition metal, and E_{C_2N-NCM} represents the energy of C_2N-NCM substrate. A negative Eb value indicates that the binding of the TM atom to C_2N-NCM is energetically stable.

The adsorption energy (E_{ads}) of adsorbates was calculated as follows:

$$E_{ads} = E_{total} - E_{adsorbate} - E_{substrate} \tag{2}$$

Where E_{total}, $E_{adsorbate}$, and $E_{substrate}$, represent the total energy of the adsorbed systems, the isolated adsorbate, and the isolated substrate, respectively. According to this formulation, a more negative value of adsorption energy indicates a stronger adsorption.

The Gibbs free energy change (ΔG) between the two states during the N_2 reduction reaction was calculated according to the computational hydrogen electrode (CHE) model proposed by Nørskov et al. The free energy of the electron-proton pair ($H^+ + e^-$) can be referenced to the chemical potential of gaseous H_2 at equilibrium (0V vs standard hydrogen electrode). The calculation formula is as follows:

$$\Delta G = \Delta E + \Delta E_{ZEP} - T\Delta S + \Delta G_U + \Delta G_{pH} \tag{3}$$

where ΔE is the energy difference between two states calculated by DFT method. ΔE_{ZEP} and ΔS are the zero-point energy and entropy changes between reactants and products calculated by vibration frequency at room temperature (T= 298.15 K), respectively. ΔG_U is equal to $-eU$, where e is the number of transferred electrons and U is the applied electrode potential. ΔG_{pH} is the free energy correction of pH and can be calculated by $\Delta G_{pH} = k_B T \times pH \times ln\ 10$. Because the free energy change between any two states is not affected by the pH value, the pH is set to zero in this work.

To illustrate the energy changes at different potentials, we performed nine independent calculations with system charge from −2e to +2e in a step of 0.5e. The electric potential of electrochemical interface was changed by adjusting the work function. It could be calculated by

$$U = W_f - 4.60 \tag{4}$$

where U is electrode potential referenced to standard hydrogen electrode (SHE); W_f is the work function and 4.60 is the work function of H_2/H^+ at standard conditions.

The differential charge density ($\Delta\rho$) of the substrate with adsorbed N_2 was as follows:

$$\Delta\rho = \rho_{substrate+N_2} - \rho_{substrate} - \rho_{N_2} \tag{5}$$

where $\rho_{substrate+N_2}$, $\rho_{substrate}$ and ρ_{N_2} represent the charge density of the substrate with adsorbed N_2, the substrate, and the N_2, respectively.

We use three binary features represented as one-hot encoding: the end-on mode of the first step protonation(S_{1E}), the side-on mode of the first step protonation(S_{1S}), and the final step protonation(S_6). These three cases are represented as (1,0,0), (0,1,0), and (0,0,1), respectively. This encoding method allows the model to clearly distinguish and learn the reaction characteristics under these different conditions.

Supplementary Table 1. The adsorption energy (E_{ads}) of adsorbates N_2 and N-N bond length through end-on and side-on adsorption.

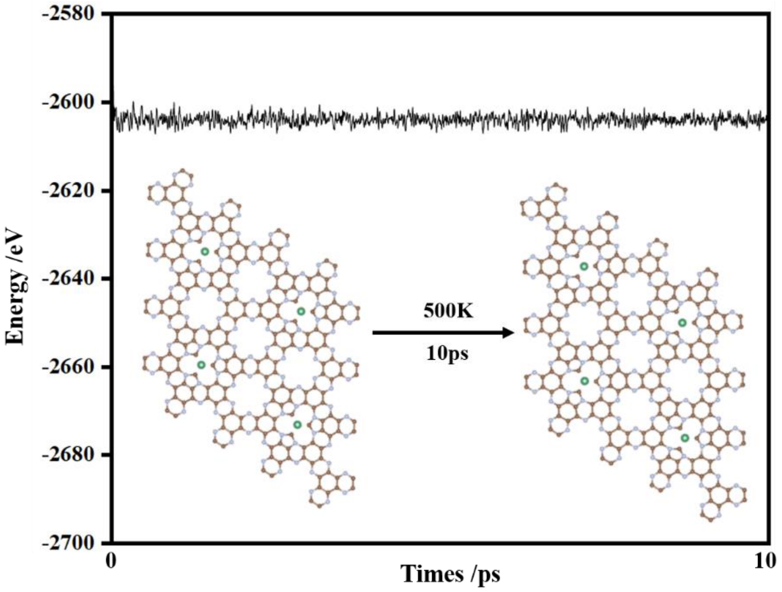
TM@C_2N-NCM	**E_{ads}/eV (side-on)**	**E_{ads}/eV (end-on)**	**N-N bond length/ Å (side-on)**	**N-N bond length/Å (end-on)**
Sc	-0.42	-0.45	1.162	1.123
Ti	-0.89	-0.99	1.177	1.140
V	-0.91	-1.02	1.175	1.137
Cr	-1.20	-1.12	1.180	1.141
Mn	-1.25	-0.99	1.174	1.135
Fe	-0.66	-1.28	1.163	1.136
Co	-0.39	-0.96	1.174	1.133
Ni	-0.37	-0.85	1.150	1.116
Cu	-0.15	-0.66	1.132	1.126
Zn	—	-0.31	—	1.099
Y	-0.50	-0.55	1.155	1.133
Zr	-0.94	-0.80	1.177	1.138
Nb	-0.93	-1.03	1.187	1.139
Mo	-0.90	-1.14	1.174	1.139
Ru	—	-1.04	—	1.131
Rh	-0.45	-0.96	1.165	1.128
Pd	-0.24	-0.49	1.148	1.128
Ag	-0.22	-0.59	1.133	1.124
Cd	—	-0.35	—	1.115
Hf	-1.18	-1.05	1.184	1.144
Ta	-1.35	-1.27	1.190	1.144
W	-1.27	-1.38	1.192	1.143
Re	-1.07	-1.44	1.185	1.141
Os	-0.70	-1.33	1.161	1.135
Ir	-0.60	-1.19	1.192	1.132
Pt	-0.21	-0.51	1.163	1.135
Au	—	-0.51	—	—
Hg	—	-0.19	—	1.117

Supplementary Table 2. Features selection and abbreviations in machine learning

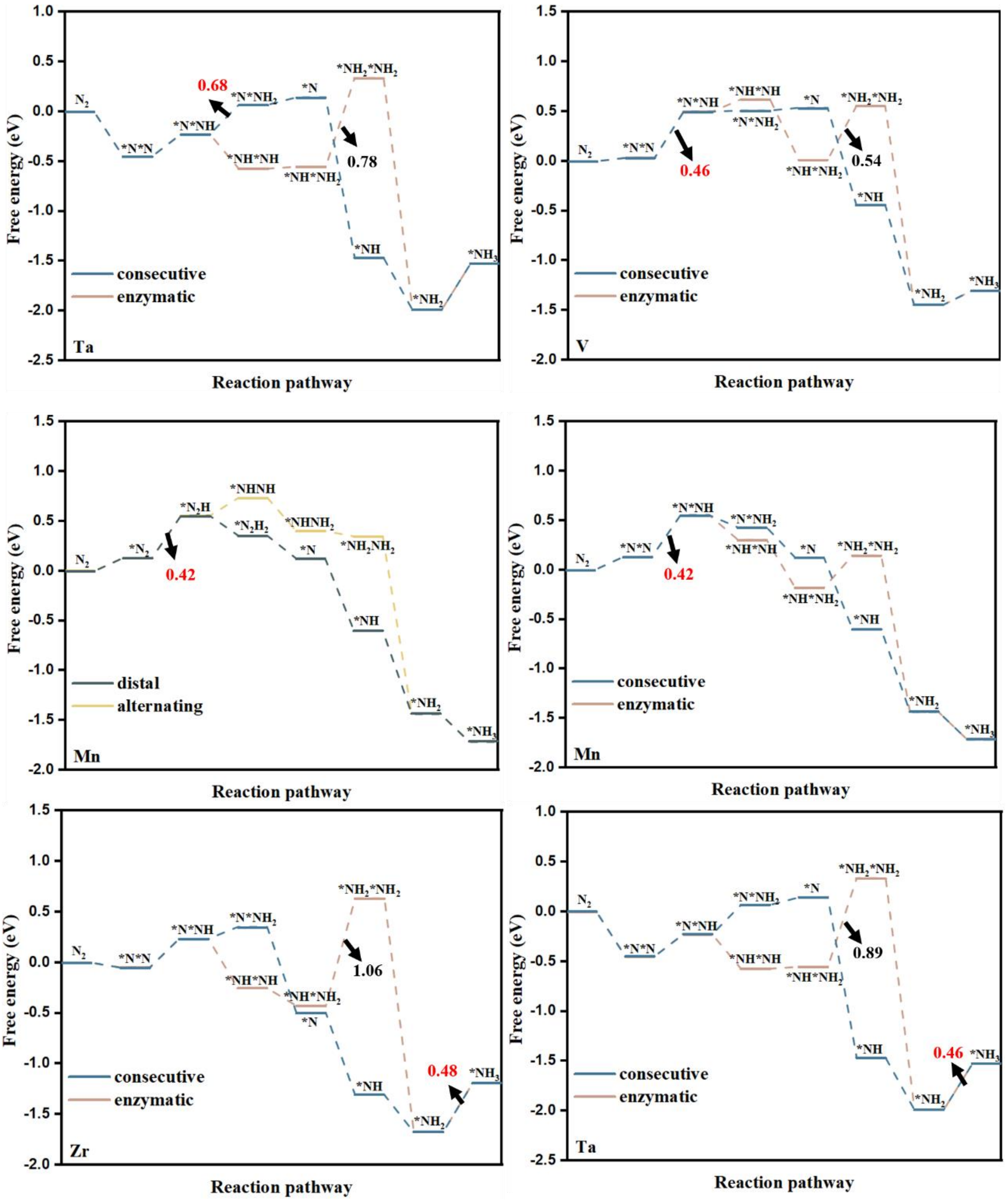
Features	Abbreviations
End-on mode of the first step protonation	S_{1E}
Side-on mode of the first step protonation	S_{1S}
Final step protonation	S_6
Pauling electronegativity of the absorbed metal atom	χ_P
Electron number of the outermost d orbital of the absorbed metal atom	N_d
Electron affinity of the absorbed metal atom	EA
1st ionization energy of the absorbed metal atom	IE
Atomic number of the absorbed metal atom	Z
Covalent radius of the absorbed metal atom	R_{cov}
Thermal conductivity of the absorbed metal atom	λ
Electrical conductivity of the absorbed metal atom	σ
Mendeleev number of the absorbed metal atom	N_m
Group of the absorbed metal atom	G
Relative atomic mass of the absorbed metal atom	Ar
Molar volume of the absorbed metal atom	V_m
s orbital radius of the absorbed metal atom	R_s
d orbital radius of the absorbed metal atom	R_d
Observed radius of the absorbed metal atom	R_o
Calculated radius of the absorbed metal atom	R_c
Van der Waals radius of the absorbed metal atom	R_v

Supplementary Table 3. Optimal feature set for machine learning

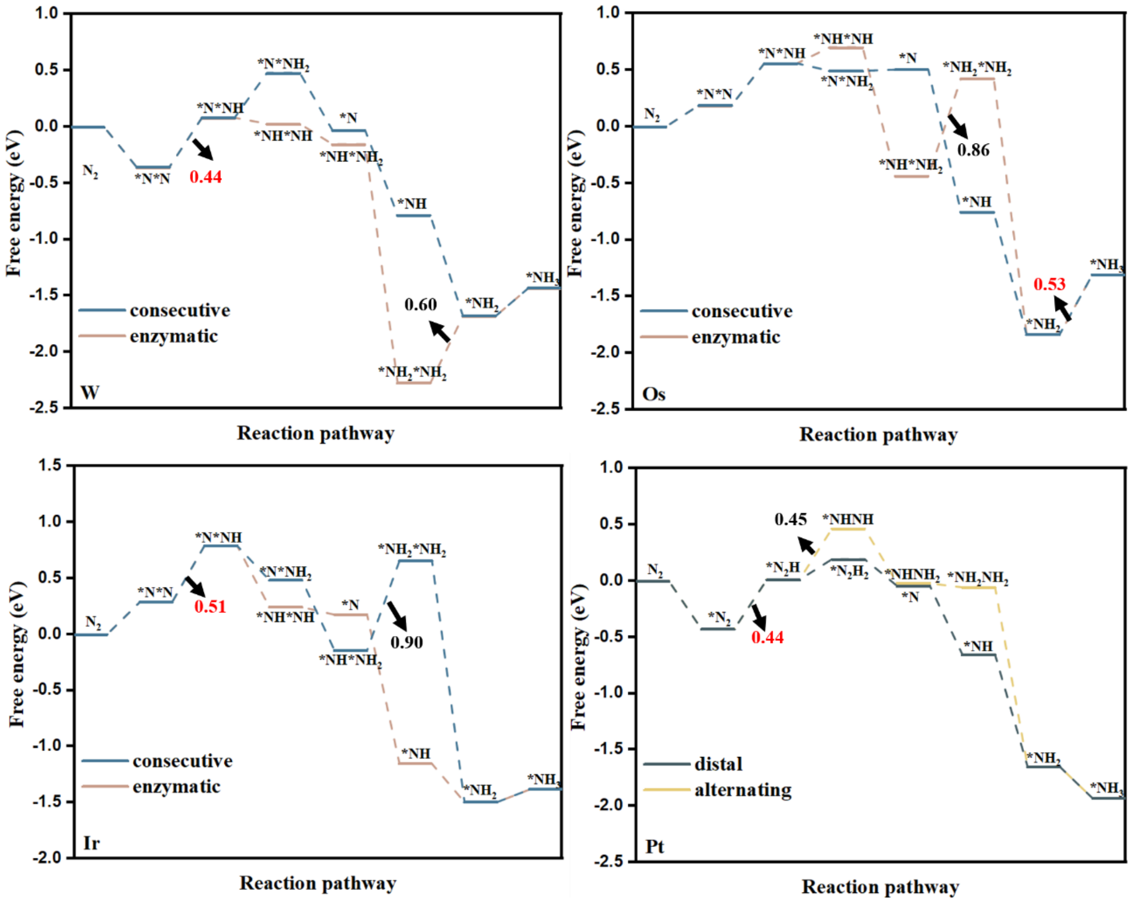
Features	Abbreviations
End-on mode of the first step protonation	S_{1E}
Final step protonation	S_6
Pauling electronegativity of the absorbed metal atom	χ_P
Electron number of the outermost d orbital of the absorbed metal atom	N_d
Electron affinity of the absorbed metal atom	EA
1st ionization energy of the absorbed metal atom	IE
Atomic number of the absorbed metal atom	Z
Calculated radius of the absorbed metal atom	R_c
Thermal conductivity of the absorbed metal atom	λ
Mendeleev number of the absorbed metal atom	N_m
Van der Waals radius of the absorbed metal atom	R_v



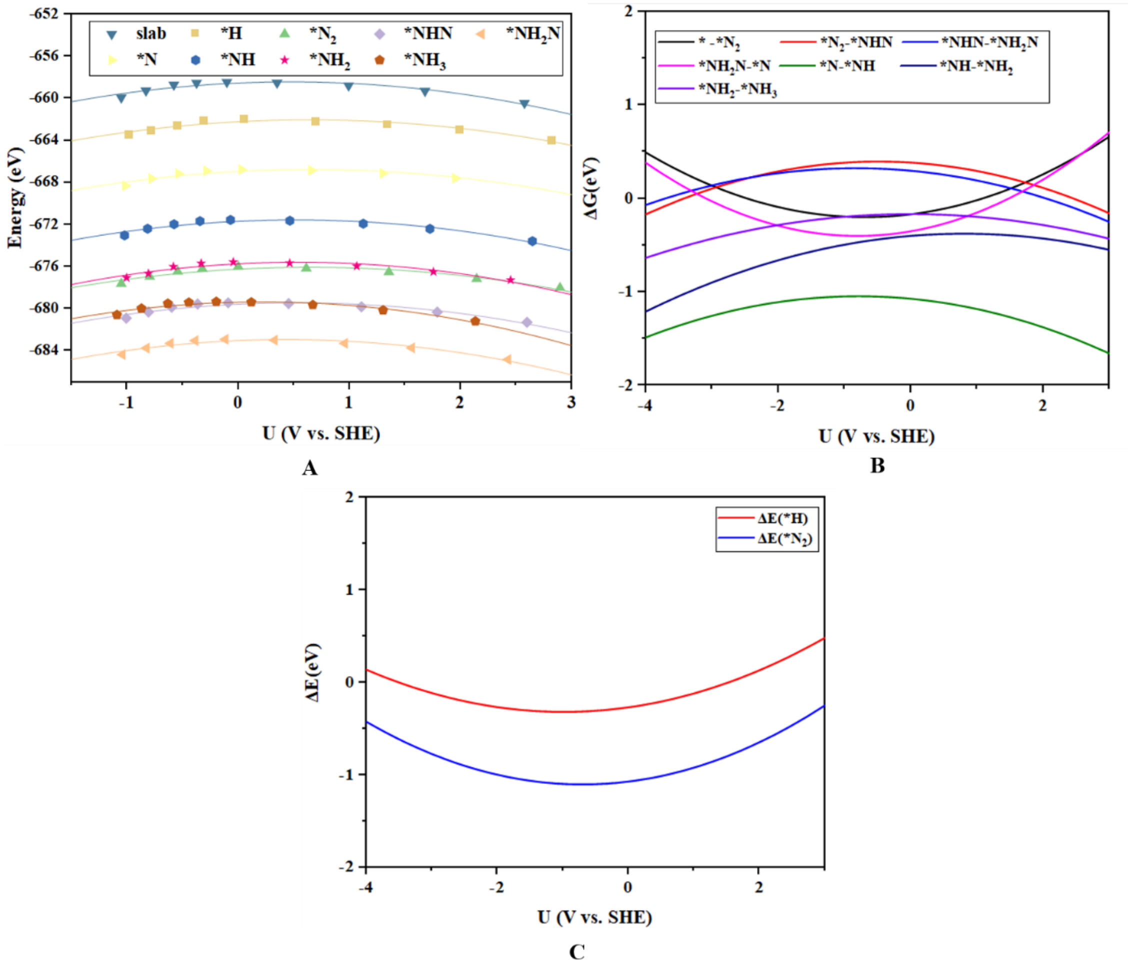
Supplementary Figure 1. Energy fluctuations over time during AIMD simulations of Nb@C_2N-NCM, performed at 500 K for 10 ps with a 1 fs time step.



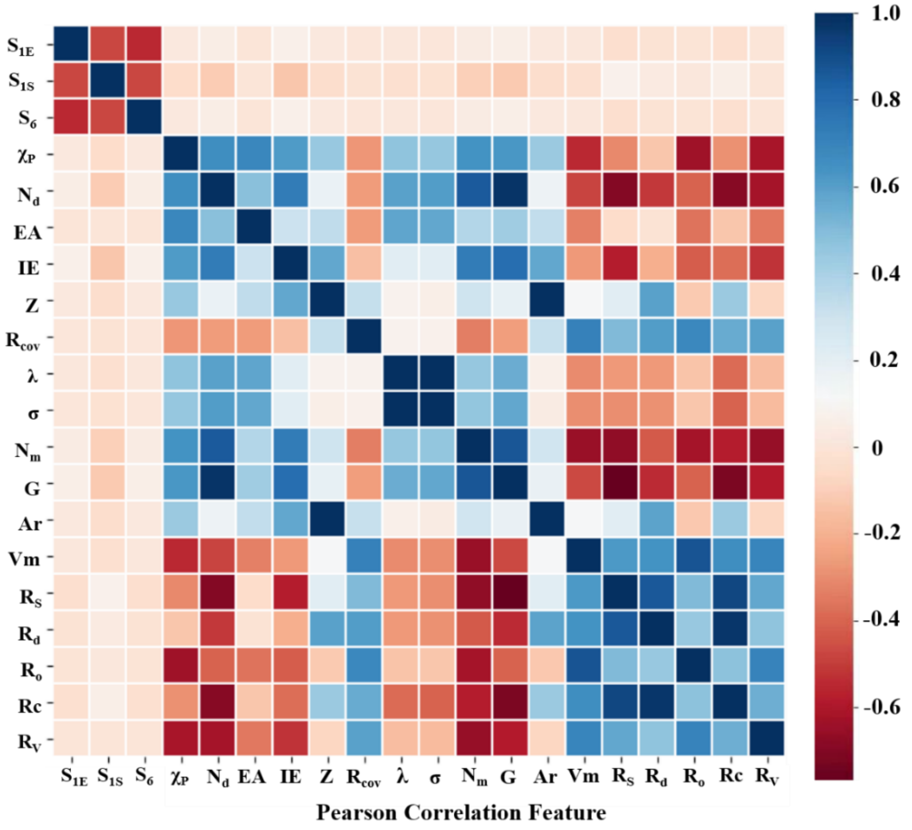
Supplementary Figure 2.1 Calculated free energy diagrams for NRR through enzymatic and consecutive mechanism catalyzed by Ti@C_2N-NCM, V@C_2N-NCM, Mn@C_2N-NCM, Zr@C_2N-NCM, Ta@C_2N-NCM. W@C_2N-NCM, Os@C_2N-NCM, Ir@C_2N-NCM. Distal and alternating mechanism catalyzed by Mn@ C_2N-NCM, Pt@ C_2N-NCM.



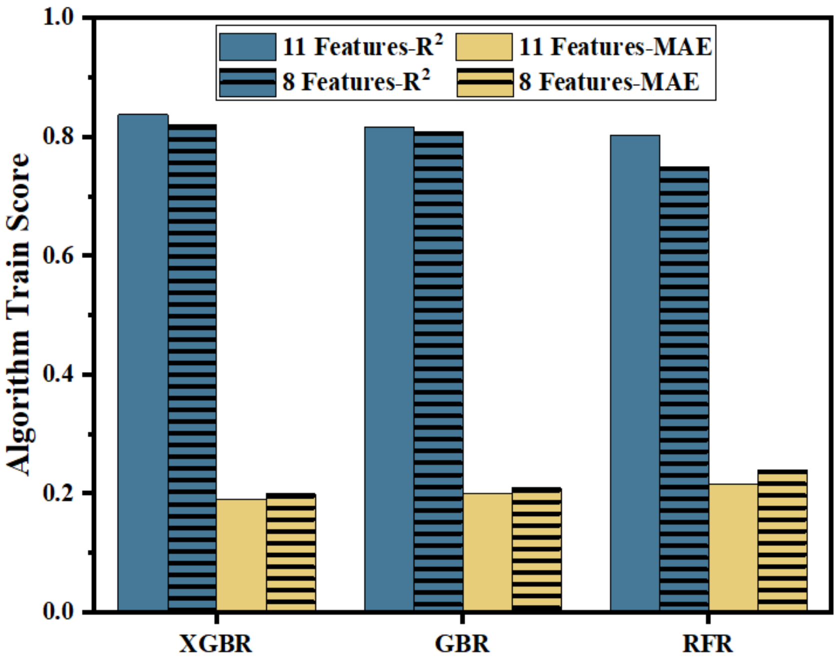
Supplementary Figure 2.2 Calculated free energy diagrams for NRR through enzymatic and consecutive mechanism catalyzed by Ti@C_2N-NCM, V@C_2N-NCM, Mn@C_2N-NCM, Zr@C_2N-NCM, Ta@C_2N-NCM. W@C_2N-NCM, Os@C_2N-NCM, Ir@C_2N-NCM. Distal and alternating mechanism catalyzed by Mn@ C_2N-NCM, Pt@ C_2N-NCM.



Supplementary Figure 3 A: Computed energies of the Nb@C_2N-NCM and corresponding reaction intermediates as a function of the applied electrode potential (SHE); B: Free energy changes of the reaction steps of Nb@C_2N-NCM as a function of potential. C: The adsorption energies of N_2 and H as a function of potential.



Supplementary Figure 4. Pearson correlation feature of 20 types of features



Supplementary Figure 5. Comparison of the average training scores using 11 and 8 features.