

Supporting Information

Structural Rule of Heteroatom-Modified Single-Atom Catalysts for CO₂ Electroreduction Reaction

Xinyuan Sui^a, Haiyang Yuan^{*a}, Yu Hou^{*a}

^aKey Laboratory for Ultrafine Materials of Ministry of Education, Shanghai Engineering Research Center of Hierarchical Nanomaterials, School of Materials Science and Engineering, East China University of Science and Technology, Shanghai 200237, China.

*Emails: yhou@ecust.edu.cn; hyyuan@ecust.edu.cn

Note S1. Calculation for the dissolution potentials (U_{diss}) of SACs

To assess the feasibility of SACs in electrochemical environment, we examined their electrochemical stabilities by quantitatively calculating the dissolution potentials (U_{diss}):

$$U_{\text{diss}} = U_{\text{diss}}^0 - E_f / (n * e) \quad (1)$$

where U_{diss}^0 is the standard dissolution potential for metal from experiments¹, and n is the number of electrons involved in the electrochemical dissolution process. E_f is the formation energy of SACs, which can be calculated utilizing the following formula:

$$E_f = E_b - E_c = E_{\text{M-Sub}} - E_{\text{Sub}} - E_{\text{M}} - E_c \quad (2)$$

In this formula, E_b and E_c represent the binding energies of metal center and substrate, and the cohesive energy of metal, respectively. $E_{\text{M-Sub}}$, E_{Sub} , and E_{M} represent the energies of the substrate with single metal atom anchored, pure substrate and single metal atom, respectively. A larger dissolution potential represents a greater electrochemical stability.

Note S2. Calculation for the Gibbs free energy change of reaction steps in CO₂RR

The electrochemical conversion of CO₂ into CO (CO₂RR) is a process involving the transfer of two proton-coupled electron pairs whose four elementary steps can be written as:



In this process, there are three key intermediates (*CO₂, *COOH and *CO). Here, we calculated the adsorption energies of the key intermediates in the CO₂RR process with the formula: $E_{\text{ads}}(X) = E_{X/\text{surf}} - E_{\text{surf}} - E_X$, where $E_{X/\text{surf}}$, E_{surf} and E_X represent the energies of the surface with adsorbates, the clean substrate, and adsorbates, respectively. For *COOH, $E_{\text{ads}}(*\text{COOH})$ was calculated by reference to the energies of CO₂ and 1/2H₂ according to the computational hydrogen electrode (CHE) model. The more negative $E_{\text{ads}}(X)$ indicates the stronger binding strength between adsorbates and the surface.

The Gibbs free energy changes (ΔG) of elementary steps in CO₂RR were calculated using the CHE model. In this approach, the chemical potentials of a proton-electron pair (H⁺/e⁻) and half H₂ molecule are equilibrated at 0 V (vs. the reversible hydrogen electrode, RHE) at all pH values^{2, 3}. The effect of the potential on the state with an electron involved was considered by shifting the energy of $-eU$. Therefore, after obtaining the adsorption energy of the key intermediates, the corresponding Gibbs free energy change (ΔG_i) of each elementary step in CO₂RR at the potential U can be calculated as follows:

$$\Delta G_1 = E(*\text{CO}_2) - E(*) - E(\text{CO}_{2(\text{g})}) + (\Delta E_{\text{ZPE}} - T\Delta S) \quad (5)$$

$$= E_{\text{ads}}(*\text{CO}_2) + (\Delta E_{\text{ZPE}} - T\Delta S)$$

$$\Delta G_2 = E(*\text{COOH}) - E(*\text{CO}_2) - E(\text{H}_2)/2 + (\Delta E_{\text{ZPE}} - T\Delta S) + eU \quad (6)$$

$$= E_{\text{ads}}(*\text{COOH}) - E_{\text{ads}}(*\text{CO}_2) + (\Delta E_{\text{ZPE}} - T\Delta S) + eU$$

$$\Delta G_3 = E(*\text{CO}) + E(\text{H}_2\text{O}) - E(*\text{COOH}) - E(\text{H}_2)/2 + (\Delta E_{\text{ZPE}} - T\Delta S) + eU \quad (7)$$

$$= E_{\text{ads}}(*\text{CO}) - E_{\text{ads}}(*\text{COOH}) + (\Delta E_{\text{ZPE}} - T\Delta S) + \Delta G_0 + eU$$

$$\Delta G_4 = E(*) + E(\text{CO}_{(\text{g})}) - E(*\text{CO}) + (\Delta E_{\text{ZPE}} - T\Delta S) \quad (8)$$

$$= -E_{\text{ads}}(*\text{CO}) + (\Delta E_{\text{ZPE}} - T\Delta S)$$

where $E_{\text{ads}}(*\text{CO}_2)$, $E_{\text{ads}}(*\text{COOH})$ and $E_{\text{ads}}(*\text{CO})$ are the adsorption energies of *CO₂, *COOH and *CO, and ΔG_0 is the Gibbs free energy of CO₂RR to CO from the experiment (CO₂ + H₂ → CO + H₂O, $\Delta G_0 = 0.67$ eV). ΔE_{ZPE} and $T\Delta S$ are the differences of the zero-point energy and entropic contributions, which result from the experimental data and vibrational frequency calculations at 298 K. The reaction maximum Gibbs free energy ($\Delta G_{\text{max}}[\text{CO}_2\text{RR}]$) of the elementary steps in CO₂RR is often used to evaluate the intrinsic activities of catalysts, which can be written as $\Delta G_{\text{CO}_2\text{RR}} = \max \{\Delta G_1, \Delta G_2, \Delta G_3, \Delta G_4\}$. The smaller $\Delta G_{\text{CO}_2\text{RR}}$ means the better CO₂RR activity of catalyst.

Regarding the effect of the solution, we employed the explicit solvation model on SACs, where 20 H₂O molecules were applied above the surface as an initial aqueous network at the liquid/solid interface (Fig. S4). First, we performed the ab initio molecular dynamics (AIMD) simulation of the H₂O structure on SACs (Fig. S4). Only the Γ -point was used to sample the Brillouin zone. The simulation temperature was set to 300 K with a 1 fs movement for each step in the canonical (NVT) ensemble employing Nosé-Hoover thermostats. We selected the H₂O structure from the stabilized MD simulations (small fluctuation in energy after MD simulations), and then optimized intermediates adsorbed on SACs to obtain the total energy (E_{tot}) of each structure with this H₂O structure involved. Considering that the solution structures of the water network on different SACs after optimization could change, which may still affect E_{tot} , we deducted the contribution of the

water solution in E_{tot} but still considered the solvation effect for each sample as follows: (i) we calculate the total energy of the water solution ($E_{\text{H}_2\text{O}}$) in the optimized structures; (ii) we deduct $E_{\text{H}_2\text{O}}$ from E_{tot} to obtain the solvation-included energy of each structure (ΔE): $\Delta E = E_{\text{tot}} - E_{\text{H}_2\text{O}}$.

Table S1. The specific applied U-J value (U_{eff}) of 3d metals for DFT calculations⁴.

3d	Mn	Fe	Co
U_{eff}	3.06	3.29	3.42

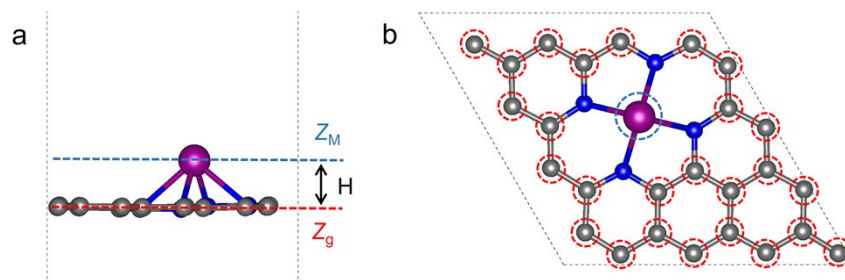


Fig. S1 Scheme for calculating the height (i.e., H) of the metal center above the graphene surface. The graphene surface is chosen as the benchmark to calculate the height (i.e., H) of the metal center. Due to the structural relaxation, the positions of C atoms in the graphene could change to a certain extent. We averaged the z-coordinates of all C atoms in the graphene (denoted as Z_g), and then calculated the difference between Z_g and the z-coordinate (Z_M) of metal center as the height (i.e., H) of the metal center above the graphene surface ($H = Z_M - Z_g$).

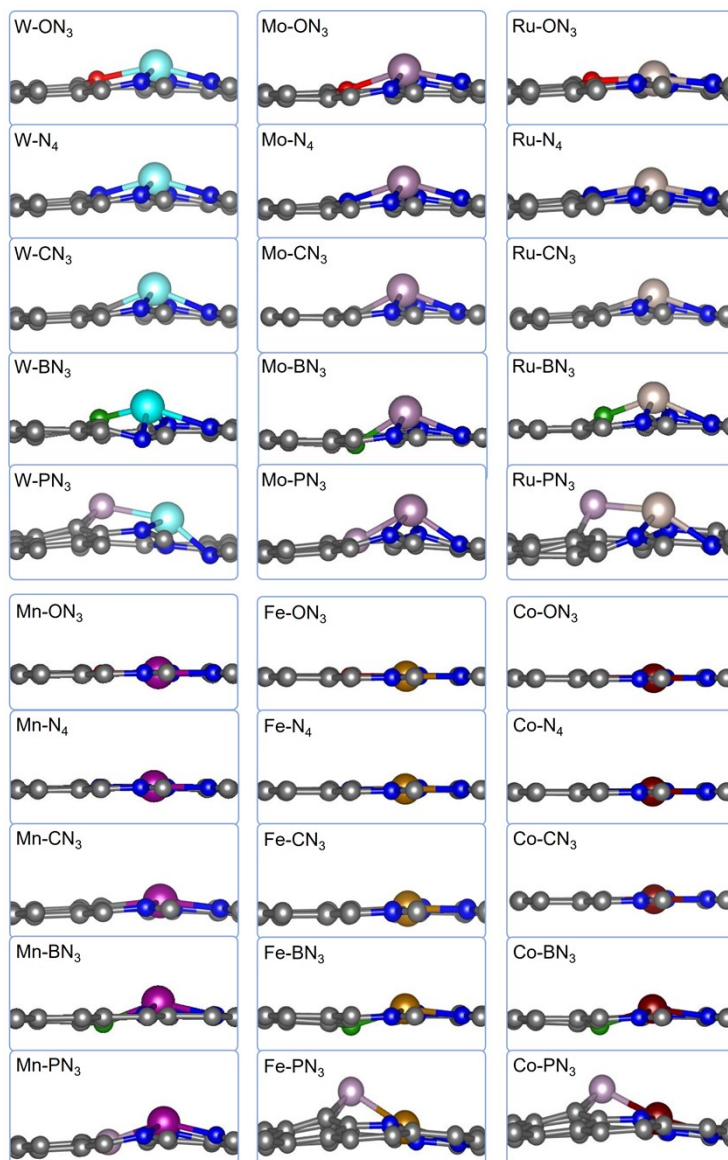


Fig. S2 Configuration of each M-XN₃ SACs (M = W, Mo, Ru, Mn, Fe and Co and X = O, N, C, B and P).

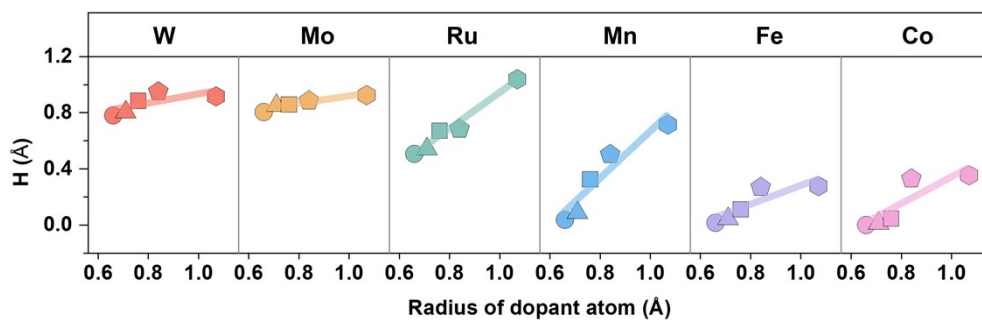


Fig. S3 Linear relationships between the height (i.e., H) of the metal center above the graphene surface and the radius of the ligand X atom on different SACs.

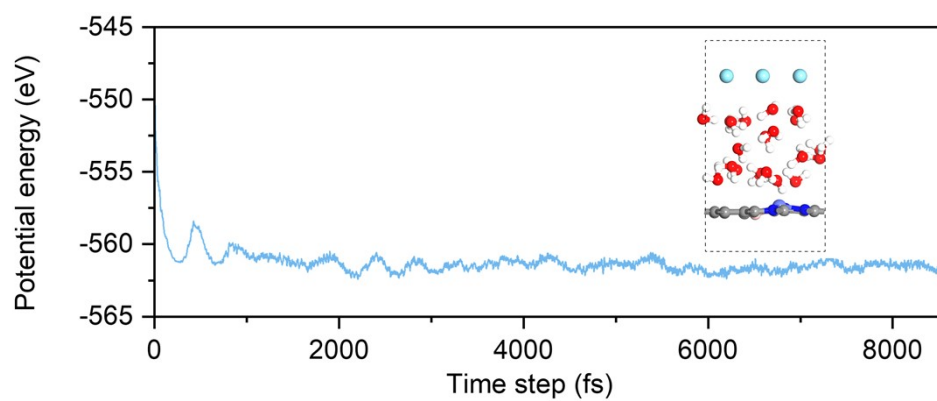


Fig. S4 Explicit solvation model (20 H₂O molecules) upon SACs and the potential energy variation from its corresponding AIMD simulation.

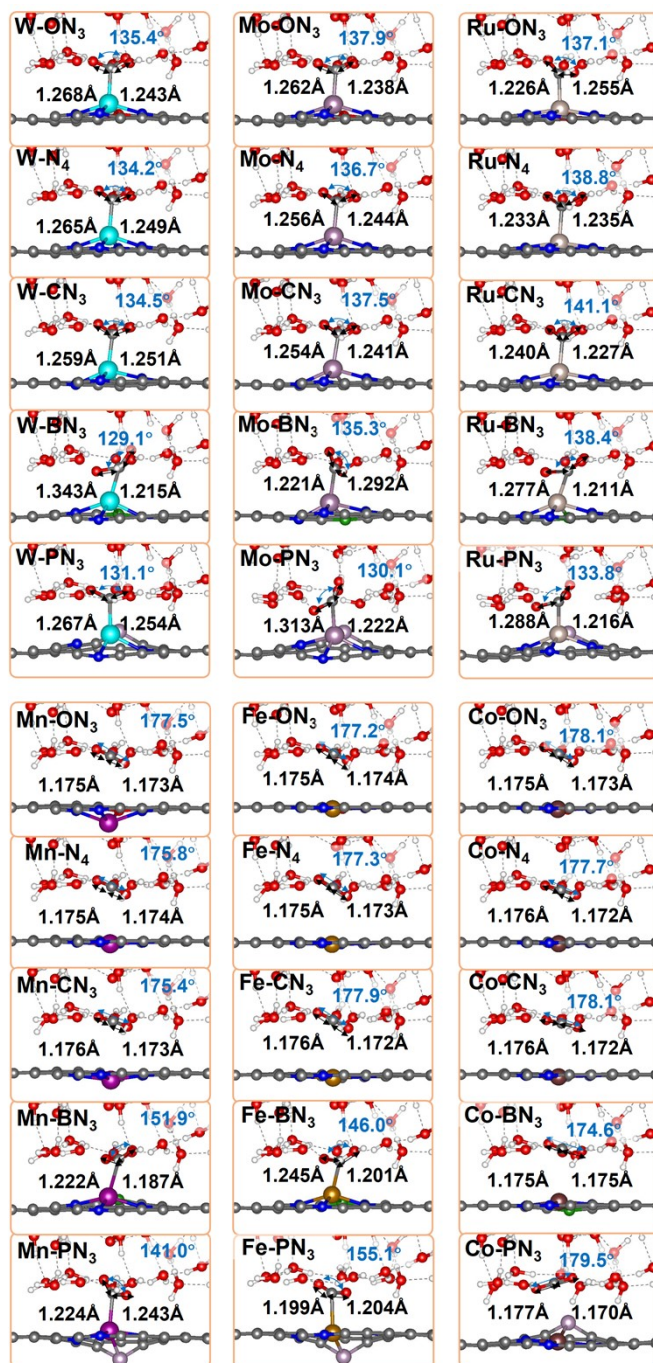


Fig. S5 Adsorption configuration of CO₂ on each M-XN₃ SACs.

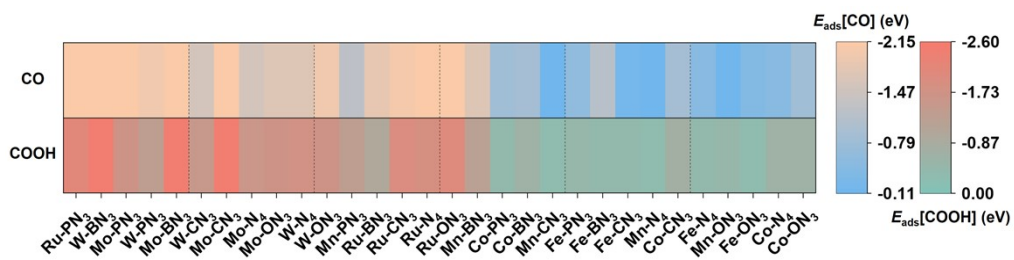


Fig. S6 Adsorption energies of CO and COOH on each M-XN₃ SACs.

Reference

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