

# Decoding CO<sub>2</sub> Adsorption Modes and CO Yield Variation on TM–N<sub>4</sub> Single-Atom Catalysts via Constant-Potential Computation and Machine-Learning Investigation

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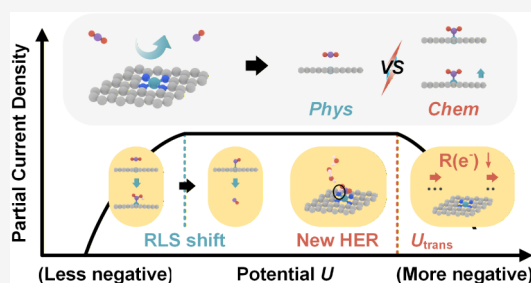
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**ABSTRACT:** Transition metal-based TM–N<sub>4</sub> single-atom catalysts (SACs) are promising materials for electrochemical CO<sub>2</sub> reduction reactions (CO<sub>2</sub>RR) toward CO formation. In this study, we employed the constant-potential method to investigate CO<sub>2</sub> adsorption and reduction on 10 TM–N<sub>4</sub> SACs (TM = Sc–Zn), with a particular focus on Ni–N<sub>4</sub>. We first evaluated the CO<sub>2</sub> adsorption mode on the TM active site as a function of the applied electrode potential,  $U$ . Landau free energy analysis revealed a transition in CO<sub>2</sub> adsorption mode from physisorption ( $D_{\infty h}$ – $D_{2h}$ ) to chemisorption ( $C_{2v}$ – $C_{2v}$ ) at a critical electrode potential, referred to as the “transorption” potential ( $U_{\text{trans}}$ ). Walsh diagram and machine-learning analyses revealed significant  $\pi^*$ -orbital splitting and an unusual  $\sigma$  back-donation governing  $U_{\text{trans}}$ . We then examined the CO<sub>2</sub>RR processes by considering both adsorption modes of CO<sub>2</sub>. The transition from CO<sub>2</sub> physisorption to chemisorption modes leads to a shift in the rate-limiting step from CO<sub>2</sub> hydrogenation to CO desorption, the emergence of new active sites for competing hydrogen evolution reactions, and a decrease in electron transfer rates at more negative potentials. Taken together, these observations align with the experimental CO yield profile under increasingly negative potentials, capturing key performance trends of rise, plateau, and decline. Notably, the calculated  $U_{\text{trans}}$  values are consistent with the applied potentials at which CO yield declines for five SACs for which experimental data are available (Mn, Fe, Ni, Cu, and Zn). Thus, this work establishes  $U_{\text{trans}}$  as a novel predictive parameter for CO yield performance and offers valuable guidance for the design of advanced SACs in future studies.



## INTRODUCTION

With escalating global energy demand and the urgent need to mitigate CO<sub>2</sub> emissions, converting CO<sub>2</sub> into value-added chemicals presents a viable and sustainable approach for carbon recycling.<sup>1–6</sup> Among available strategies, the electrochemical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) provides an efficient and cost-effective means of harnessing electrical energy to transform CO<sub>2</sub> into useful products such as CO, HCOOH, CH<sub>2</sub>O, CH<sub>3</sub>OH, and CH<sub>4</sub>. Since copper was first recognized as an effective CO<sub>2</sub>RR electrocatalyst,<sup>7</sup> intensive efforts have broadened the search to other transition metals (TMs) to improve reaction activity and selectivity.<sup>8–10</sup> More recently, single-atom catalysts (SACs) have drawn increasing attention due to their well-defined active sites, near-unity metal utilization efficiency, and highly tunable electronic structures.<sup>11–14</sup>

Among single-atom architectures, TM–N<sub>4</sub> SACs, in which each TM atom is coordinated by four N atoms within a graphene matrix, have emerged as promising platforms for CO<sub>2</sub>RR-to-CO conversion.<sup>15–18</sup> Progress has been propelled by synergistic theory-experiment advances: the earliest density functional theory (DFT) study identified Rh–N<sub>4</sub> as a viable

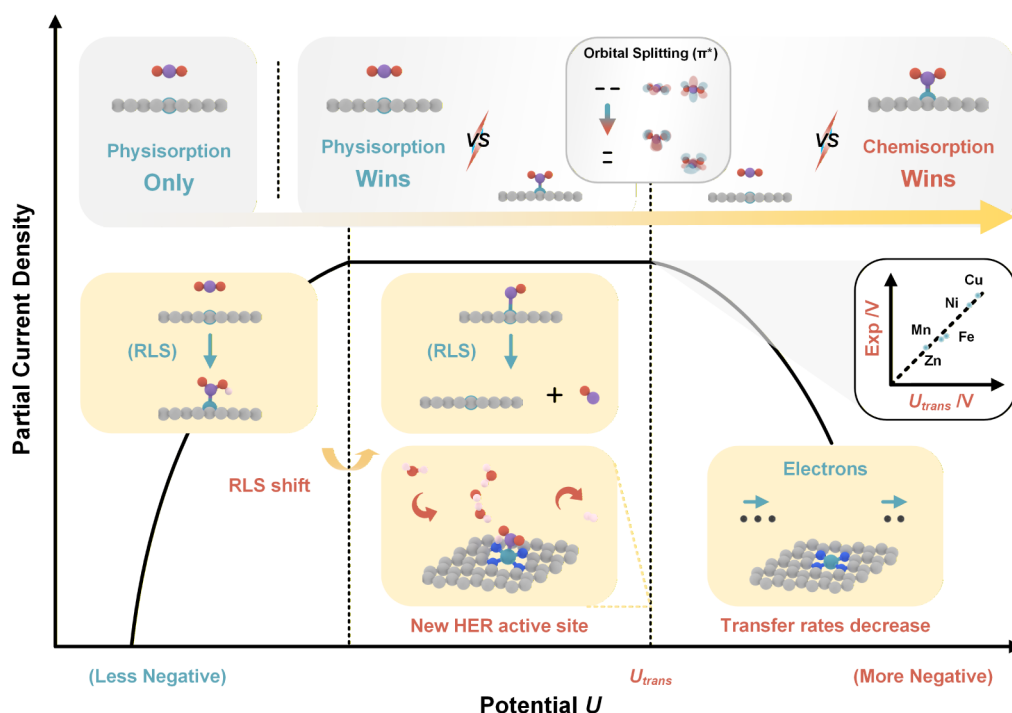
CO<sub>2</sub>RR catalyst,<sup>19</sup> and subsequent experiments confirmed the catalytic potential of TM–N<sub>4</sub> SACs, highlighting Ni–N<sub>4</sub> for its high CO selectivity.<sup>20–25</sup> Despite many DFT investigations into Ni–N<sub>4</sub> behavior, significant gaps remain in mechanistic understanding and in reconciling theoretical predictions with experimental performance metrics, particularly regarding potential-dependent adsorption modes and rate-limiting steps (RLS).

A central challenge is to resolve the CO<sub>2</sub>RR mechanism on Ni–N<sub>4</sub> SAC, specifically, the operative CO<sub>2</sub> adsorption mode and the true RLS.<sup>16</sup> Most prior theoretical studies utilized the constant charge (CC) approach in conjunction with the computational hydrogen electrode (CHE) model,<sup>26–28</sup> which typically favors CO<sub>2</sub> physisorption on Ni–N<sub>4</sub> and assigns the

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**Figure 1.** Schematics of competing CO<sub>2</sub> adsorption modes and CO partial current density (PCD) as a function of electrode potential  $U$ . The PCD curve exhibits trends of rise, plateau, and decline as the applied potential  $U$  shifts from less negative to more negative values. These trends are driven by the shift in RLS, the emergence of new active sites for competing hydrogen evolution reactions (HER), and the decrease in electron transfer rates. The observed trends were extracted from a comprehensive experimental data set, which reveals the sequential rise, plateau, and eventual decline in performance (Figure S1). The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Ni atoms are shown in blue, red, pink, and cyan, respectively. Electrons are shown as black dots.

\*COOH formation to a coupled electron–proton transfer (CEPT:  $* + \text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow *\text{COOH}$ ) pathway.<sup>29–32</sup> However, the CC/CHE framework couples electron transfer (ET) and proton transfer (PT) on a physisorbed CO<sub>2</sub> state and therefore neglects the CO<sub>2</sub> chemisorption and the stepwise, decoupled ET and PT route (DEPT:  $* + \text{CO}_2 \rightarrow *\text{CO}_2$ ;  $*\text{CO}_2 + \text{H}^+ + \text{e}^- \rightarrow *\text{COOH}$ ).<sup>8,14,33–37</sup> Together with the fixed Fermi level in the CC framework, the treatment overestimates the free-energy change for \*COOH formation ( $\sim 1.8$  eV) and artificially promotes it as the RLS.

In contrast to the widely used CC method, the constant potential (CP) approach explicitly captures potential-dependent Fermi-level shifts and interfacial electron transfer under working electrochemical conditions.<sup>17,38–42</sup> Early CP studies on Ni–N<sub>4</sub> suggested that the reaction initiates with CO<sub>2</sub> physisorption, and \*COOH formation is identified as the RLS.<sup>38,43</sup> In contrast, more recent research indicates that cation effects can shift the CO<sub>2</sub> adsorption mode toward chemisorption, enabling a DEPT pathway.<sup>44</sup> On a Fe–N<sub>4</sub> SAC, both the adsorption mode and the RLS were found to vary with applied potential and ligand environment.<sup>45</sup> These divergent findings indicate that the CO<sub>2</sub>RR mechanism is strongly potential-dependent, underscoring the need for a more consistent mechanistic picture for Ni–N<sub>4</sub> and related SACs.

Another challenge is to reconcile DFT predictions with experiments to achieve a comprehensive understanding of CO<sub>2</sub>RR performance. Two metrics are commonly used: CO selectivity (based on Faradaic efficiency) and CO yield (derived from the CO partial current density, PCD). Note that their optima often occur at different electrode potentials.

For example, in the case of Ni–N<sub>4</sub> SAC, peak selectivity typically appears near  $\sim -0.7$  V vs. reversible hydrogen electrode (RHE), whereas the maximum CO yield spans a broader potential plateau from  $\sim -1.0$  V to  $\sim -1.6$  V vs. RHE. While the absolute CO yield scales with the number of active sites, the potential-dependent trend, such as the rise, the plateau, and overall shape of the yield curve, tends to be characteristic of a given TM. Although recent DFT studies have provided valuable insights into CO–H<sub>2</sub> selectivity,<sup>46</sup> the variation of CO yield with potential has received far less attention. Therefore, a deeper understanding of CO yield is essential to capture catalytic performance and to guide the rational design of improved SACs.

In this work, using the fully converged constant-potential (FCP) method within the grand canonical ensemble, we investigated how applied electrode potential governs CO<sub>2</sub> adsorption mode transitions and CO yield on 3d TM–N<sub>4</sub> SACs. As depicted for Ni–N<sub>4</sub> in Figure 1, we found that the applied potential,  $U$ , tunes the competition between CO<sub>2</sub> physisorption and chemisorption. Walsh diagrams, together with machine-learning (ML) analysis, elucidate the accompanying electronic structure evolution. We introduced the concept of “transorption” potential ( $U_{trans}$ ) that marks the crossover at which CO<sub>2</sub> chemisorption becomes thermodynamically more favorable than physisorption. To rationalize the experimentally observed CO yield profile (Figure S1), we identified three key factors: a shift of the rate-limiting step (\*COOH formation  $\rightarrow$  CO release), the emergence of new HER active sites after chemisorption, and a decrease in electron transfer rates at high overpotentials. Notably, the calculated  $U_{trans}$  values coincide with the experimental

potentials at which the CO yield begins to decline. Leveraging this correlation, we propose  $U_{\text{trans}}$  as a DFT-derived descriptor for the design and screening of advanced SACs.

## COMPUTATIONAL METHODS

Density functional theory (DFT) calculations were conducted using the Vienna Ab initio Simulation Package (VASP).<sup>47,48</sup> The interaction between ion cores and valence electrons was described using the projector-augmented wave (PAW) method.<sup>49</sup> Exchange-correlation effects were treated using the Perdew–Burke–Ernzerhof (PBE) functional within the generalized gradient approximation (GGA).<sup>50</sup> To improve accuracy for 3d TMs, spin polarization was included and on-site Coulomb interactions were treated with the Hubbard U corrections (values in Table S1).<sup>51–53</sup> As TM–N<sub>4</sub> SACs exhibit potential-dependent spin reorganization and metastable spin manifolds,<sup>54,55</sup> multiple initial magnetic-moment configurations (Tables S2–S7) were examined for each reaction intermediate. The energetics reported in this work correspond to the lowest-energy state identified among the spin configuration examinations. Additional occupation-matrix-controlled (OMC) calculations<sup>56</sup> using different initial Ni 3d-orbital occupations further confirmed the robustness of the identified electronic states over the investigated potential range (Table S8).

The catalyst models were constructed from a (5 × 5 × 1) graphene supercell (Figure S2) with a Gamma-centered 3 × 3 × 1 *k*-points mesh for Brillouin zone sampling during structural optimizations. The plane-wave energy cutoff was set to 550 eV, and the convergence criteria were 1 × 10<sup>−5</sup> eV for electronic energy and 0.01 eV/Å for atomic forces. The lattice vector along the *z*-axis was fixed at 25 Å to ensure a large vacuum, thereby eliminating spurious interactions between periodic images. The DFT-D3 method, incorporating Becke–Johnson damping, was employed to account for van der Waals (vdW) forces, a technique commonly used in recent CO<sub>2</sub>RR studies.<sup>57,58</sup> The “accurate” precision setting was selected to reduce wrap-around errors, improving numerical stability. To accelerate convergence, we employed Gaussian smearing with a smearing width of 0.1 eV, which enhances numerical stability and ensures smooth electronic convergence for metallic systems.

The catalytic reactions under applied potentials were modeled with the FCP method within the grand canonical ensemble interfaced with VASP.<sup>59</sup> In this framework, the electron number  $N_e$  is optimized at each ionic step so that the calculated Fermi level  $E_f$  converges to the prescribed electron chemical potential  $\mu_e$ . For each trial  $N_e$ , VASP performs a conventional fixed- $N_e$  self-consistent calculation, and  $N_e$  is subsequently updated using the polynomial-fitted, damped Newton scheme until the target potential is reached. This procedure effectively allows electron exchange with an external reservoir under constant-potential conditions.

The electron chemical potential is defined as

$$\mu_e = \mu - |e|U \quad (1)$$

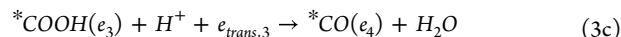
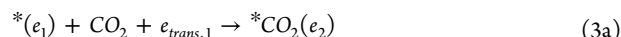
where  $\mu_e$ ,  $\mu$ , and  $U$  are the chemical potential of electrons, the work function of the standard hydrogen electrode (SHE), and the value of applied potential referenced to SHE, respectively. In this calculation, the absolute SHE work function ( $\mu$ ) value is taken as −4.44 eV.<sup>60–62</sup> All applied potentials reported in this manuscript are referenced to SHE, unless otherwise specified. Experimental potentials reported versus RHE were converted to SHE using the relevant pH values. Furthermore, continuum solvation and electrolyte screening were included in the FCP calculations using the VASPsol implicit electrolyte model,<sup>63,64</sup> in which the dielectric constant was set as 78.4 for the water solvent. Although more sophisticated nonlinear/nonlocal electrolyte models may refine absolute values, the adsorption-mode crossover is expected to remain qualitatively robust because all compared states are treated within the same CP-solvated framework.

Due to the grand-canonical treatment, the relevant energy descriptor is the Landau free energy ( $\Omega$ , also known as the grand potential). The  $\Omega$  values of reactants, intermediates, and products in the CO<sub>2</sub>RR processes were calculated as

$$\Omega = E_{\text{DFT}} + \text{ZPE} - TS - \mu_e N + E_{\text{vib}} + E_{\text{tran}} + E_{\text{rot}} \quad (2)$$

$E_{\text{DFT}}$  represents the DFT-calculated total energy, ZPE is the zero-point energy,  $TS$  is the entropic term at room temperature (298.15 K).  $N$  denotes the net excess electron number of the entire system relative to its charge-neutral reference. At each applied potential,  $N$  is adjusted self-consistently until the Fermi level matches the imposed electron chemical potential,  $\mu_e$ , of an electron reservoir. Note that  $N$  is a global property of the calculated system rather than a local adsorbate charge obtained from Bader or other charge-partitioning analyses. The  $\mu_e N$  term accounts for the energetic contribution associated with electron exchange between the simulated cell and the electron reservoir. The  $E_{\text{vib}}$ ,  $E_{\text{tran}}$ , and  $E_{\text{rot}}$  terms represent the thermal corrections associated with the vibrational, translational, and rotational energy contributions for free molecules; for adsorbates only vibrational contributions were considered. The second, third, and fifth to seventh correction terms were postprocessed with the VASP toolkit.<sup>65</sup> To reflect varying electrolyte pH values in experiments, we added the correction term  $\Delta\Omega_{\text{pH}} = RT \cdot \ln(10) \times \text{pH}$  to electrochemical steps involving proton–electron transfers, where  $R$  is the gas constant.

The CO<sub>2</sub> adsorption and reduction sequence can be represented as follows:



where  $* \text{CO}_2$ ,  $* \text{COOH}$ , and  $* \text{CO}$  denote the intermediates adsorbed on the active site  $*$ ,  $e_i$  ( $i = 1–4$ ) denotes the state-dependent electron population of the electrode/adsorbate system at the applied potential  $U$ , whereas  $e_{\text{trans},i}$  stand for the number of electrons exchanged with the external electron reservoir during the elementary step  $i$ .  $\text{H}^+$  represents the proton participating in the corresponding protonation step. Electron-number balance between successive states and the electron reservoir is given by

$$e_2 = e_1 + 16 + e_{\text{trans},1} \quad (4a)$$

$$e_3 = e_2 + e_{\text{trans},2} \quad (4b)$$

$$e_4 = e_3 + e_{\text{trans},3} - 8 \quad (4c)$$

$$e_1 = e_4 + e_{\text{trans},4} - 10 \quad (4d)$$

The corresponding Landau adsorption free energies at potential  $U$  are identified as

$$\Delta\Omega_{* \text{CO}_2} = \Omega_{* \text{CO}_2} - \Omega_{\text{CO}_2} - \Omega_* \quad (5a)$$

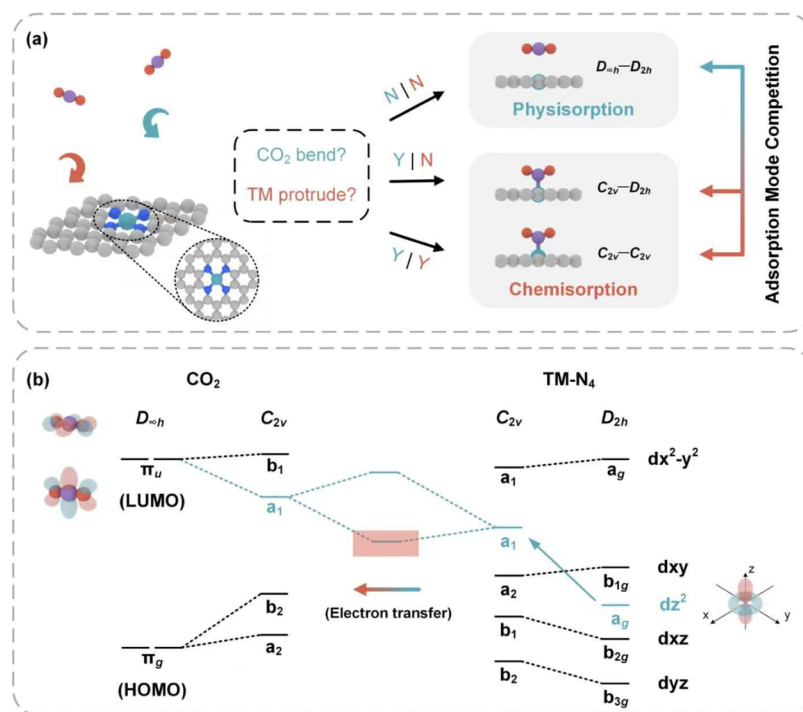
$$\Delta\Omega_{* \text{COOH}} = \Omega_{* \text{COOH}} - \Omega_{* \text{CO}_2} - \frac{1}{2}\Omega_{\text{H}_2} + eU \quad (5b)$$

$$\Delta\Omega_{* \text{CO}} = \Omega_{* \text{CO}} + \Omega_{\text{H}_2\text{O}} - \Omega_{* \text{COOH}} - \frac{1}{2}\Omega_{\text{H}_2} + eU \quad (5c)$$

$$\Delta\Omega_{\text{CO}} = \Omega_* + \Omega_{\text{CO}} - \Omega_{* \text{CO}} \quad (5d)$$

where  $\Omega_{\text{CO}_2}$ ,  $\Omega_{\text{H}_2}$ ,  $\Omega_{\text{H}_2\text{O}}$ , and  $\Omega_{\text{CO}}$  represent the Landau free energies of the free gas-phase molecules, while  $\Omega_*$ ,  $\Omega_{* \text{CO}_2}$ ,  $\Omega_{* \text{COOH}}$ , and  $\Omega_{* \text{CO}}$  denote those of the active site and adsorbed intermediates.

To evaluate the thermal stability of intermediates during the CO<sub>2</sub>RR processes, *ab initio* molecular dynamics (AIMD) simulations were conducted in the canonical (NVT) ensemble with a Nose–Hoover thermostat.<sup>66,67</sup> The system temperature was maintained at 300 K, corresponding to room temperature relevant for experimental conditions. Each trajectory ran for 10 ps with a time step of 1 fs, providing adequate sampling of dynamic fluctuations between intermediates and active centers (TM–N<sub>4</sub>). Explicit water molecules



**Figure 2.** (a) Competition of CO<sub>2</sub> adsorption modes on TM-N<sub>4</sub> SAC, including one physisorption and two chemisorptions, depending on CO<sub>2</sub> bending and TM protrusion. (b) Orbital energy level diagrams of CO<sub>2</sub> and TM-N<sub>4</sub> SAC, illustrating how symmetry changes affect orbital splitting and interaction during adsorption. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, and Ni atoms are shown in blue, red, and cyan, respectively.

were not included in AIMD calculations since their incorporation would substantially increase the computational cost; consequently, these simulations are intended to reveal qualitative trends in the finite-temperature stability, rather than to quantitatively resolve specific solvent-mediated interactions.

The AIMD calculations were performed at fixed electron number, with the total electron number initialized from the corresponding CP-DFT calculation at  $U_{\text{trans}}$  and subsequently held constant during the trajectory. These simulations were used only to evaluate the finite-temperature structural stability of the CP-derived chemisorbed states and should not be interpreted as fully grand-canonical dynamics. As an *a posteriori* check, the CO<sub>2</sub>-chemisorbed state on Ni-N<sub>4</sub> was examined by evaluating the electrode potentials inferred from snapshots along the AIMD trajectory, which showed only minor deviations from the target value (Figure S3). This treatment is also consistent with related fixed-charge strategies previously used to approximate CP energetics in electrocatalysis.<sup>68–70</sup>

Microkinetic simulations were performed with the MKMCXX program to evaluate the CO/H<sub>2</sub> selectivity.<sup>71</sup> The simulations utilized a mean-field, well-mixed surface reactor model and did not include explicit mass-transport terms. Fixed reservoir conditions were employed, in which reactants (CO<sub>2</sub> and H<sub>2</sub>O) were treated as constant external reservoirs. At  $t = 0$ , the surface was initialized with one adsorbed CO<sub>2</sub> species and four vacant sites, consistent with the site normalization used in the MKMCXX input. The coupled ordinary differential equations governing surface coverages were integrated using the deterministic SEQUENCERUN solver, with both the relative and absolute tolerances set to  $10^{-8}$  (dimensionless).

Reaction rate constants were evaluated within transition-state theory using the Eyring equation under the harmonic approximation, based on the CI-NEB barriers and free-energy corrections described above. All the transition states needed in the microkinetic simulations were determined using the climbing image nudged elastic band (CI-NEB) method.<sup>72</sup> For CI-NEB calculations, an initial water-containing configuration was generated using Packmol by placing 25 H<sub>2</sub>O molecules around the catalytic surface.<sup>73</sup> The resulting structure was then equilibrated via AIMD for 5 ps to obtain a more representative

solvation environment. After equilibration, 13 H<sub>2</sub>O molecules near the active site were retained to construct the initial and final states with explicit solvation for the subsequent CI-NEB calculations. Following structural relaxation of the initial and final states, CI-NEB calculations along the reaction pathway were carried out using a quasi-Newton algorithm with a 5.0 eV/Å<sup>2</sup> spring constant. To balance computational cost and accuracy, the force convergence threshold was set to 0.05 eV/Å, while all other convergence settings were kept identical to those used in the geometry optimizations.

To quantify material descriptors controlling  $U_{\text{trans}}$ , we employed an ML workflow based on the Sure Independence Screening and Sparsifying Operator (SISSO),<sup>74</sup> a compressed sensing symbolic regression method used to identify the physically interpretable descriptors governing the crossover from CO<sub>2</sub> physisorption to chemisorption. The initial feature pool consisted of 21 primary descriptors spanning atomic properties, bulk electronic characteristics, and surface orbital features. Models were constructed in both one-dimensional (1D) and two-dimensional (2D) descriptor spaces with a maximum expression complexity of 5. Leave-one-out cross-validation (LOOCV) was performed to assess model robustness.

## RESULTS AND DISCUSSION

### Physisorption and Chemisorption under Constant Potential

To predict CO<sub>2</sub> adsorption on TM-N<sub>4</sub> SACs under varying applied potentials, we first analyzed the symmetry characteristics of the adsorbate-catalyst ensemble. Figure 2a illustrates the possible adsorption modes, and Figure 2b summarizes the corresponding orbital interactions between CO<sub>2</sub> and TM *d*-orbitals. Free CO<sub>2</sub> is linear with *D*<sub>∞h</sub> symmetry, while a pristine, square-planar TM-N<sub>4</sub> center adopts *D*<sub>2h</sub> symmetry. In the physisorption state, CO<sub>2</sub> remains linear and interacts with the TM center mainly through van der Waals forces with negligible charge transfer, essentially preserving the *D*<sub>∞h</sub> (CO<sub>2</sub>)

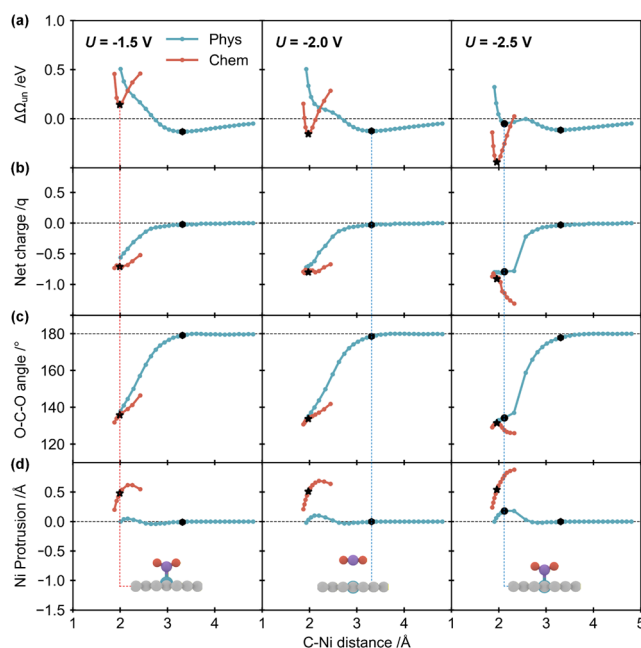


and  $D_{2h}$  (TM– $N_4$ ) symmetries. However, chemisorbed  $CO_2$  assumes bent  $C_{2v}$  symmetry, activating symmetry-allowed overlap with metal  $d$ -orbitals and enabling charge transfer. Two possible chemisorption geometries then arise: (i) planar, in which the TM atom remains nearly coplanar with the  $N_4$  ligand (site symmetry  $\sim D_{2h}$ ); and (ii) pyramidal, in which the TM atom protrudes from the  $N_4$  plane toward  $CO_2$ , lowering the site symmetry to  $C_{2v}$  and increasing orbital overlap. Therefore, potential-dependent  $CO_2$  adsorption can be viewed as a competition between one physisorption configuration and two distinct chemisorption configurations (planar vs pyramidal), whose relative stabilities are governed by symmetry and metal– $CO_2$  orbital matching.

We next systematically investigated  $CO_2$  adsorption modes across 3d TM– $N_4$  SACs under varying applied potentials, using Ni– $N_4$  SAC as a representative case due to its experimentally reported highest  $CO_2$ RR performance.<sup>20–25</sup> Beyond physisorption, we considered four possible chemisorption configurations, namely,  $\eta^1$ -C,  $\eta^1$ -O,  $\eta^2$ -C,O, and  $\eta^2$ -O,O, as shown in Figure S4. The  $\eta$  notation is used to describe the adsorption mode of  $CO_2$  on the TM center, where  $\eta^1$  indicates that only one atom is connected to the active site, and  $\eta^2$  indicates that two atoms are connected to the active site. For Ni– $N_4$ ,  $\eta^1$ -C is the only stable chemisorbed structure, corresponding to the bent  $C_{2v}$ -type state predicted from symmetry considerations, whereas the other three motifs converge to the  $\eta^1$ -C or physisorption upon geometry optimization. To ensure the stability of the lowest-energy state and avoid the metastable spin manifolds, we tested multiple initial magnetic moment configurations for each adsorption mode (Tables S2–S7) and adopted the results corresponding to the lowest energy state for the subsequent analysis. Note that though metastable manifolds exist, the lowest-energy-state ordering still preserves the physisorption  $\rightarrow$  chemisorption crossover and does not change the reported  $U_{trans}$  trend.

To clarify the  $CO_2$  adsorption landscape, we examined the potential-dependent Landau free energy profiles on Ni– $N_4$  SAC under applied potentials of  $U = -1.5$ ,  $-2.0$ , and  $-2.5$  V (vs SHE) (Figure 3a). To generate the physisorption and chemisorption curves, we began with two fully relaxed configurations: one corresponding to physisorption (where the  $CO_2$ –TM distance is around 3 Å) and the other to chemisorption (with a  $CO_2$ –TM distance of approximately 2 Å). We then calculated the adsorption energy profile as a function of  $CO_2$  adsorption height by constraining the  $z$ -coordinate of the C atom while relaxing all other degrees of freedom. This constrained-relaxation approach resulted in two distinct curves: the physisorption branch evolves from a weakly bound, nearly linear  $CO_2$  state at longer C–Ni distances, whereas the chemisorption branch originates from a bent, charge-transferred  $CO_2$  state at shorter distances.

Note that both physisorption and chemisorption branches exhibit distinct minima (Figure 3a): a physisorption minimum near  $\sim 3$  Å (marked as solid hexagon), corresponding to the  $D_{\infty h}$ – $D_{2h}$  configuration, and a chemisorption minimum near  $\sim 2$  Å (solid asterisk), associated with the  $C_{2v}$ – $C_{2v}$  configuration (*vide infra* for further details). The physisorption minimum is largely unaffected by the applied potentials. In contrast, the chemisorption minimum stabilizes progressively with increasing overpotential (more negative potentials), transitioning from an unfavorable state at  $-1.5$  V to a



**Figure 3.** (a) Landau  $CO_2$  adsorption energy profiles ( $\Delta\Omega_{un}$ ), (b) net charge transfer to  $CO_2$ , (c) O–C–O angle, and (d) Ni protrusion height as functions of the C–Ni distance for the physisorption (blue) and chemisorption (red) branches on Ni– $N_4$  at  $U = -1.5$ ,  $-2.0$ , and  $-2.5$  V vs SHE. The distinct curve shapes arise from two different  $CO_2$  adsorption pathways: the physisorption branch evolves from a weakly bound, nearly linear  $CO_2$  state at long C–Ni distances, whereas the chemisorption branch corresponds to a bent, charge-transferred  $CO_2$  state with pronounced Ni out-of-plane distortion. At  $U = -2.5$  V, a metastable chemisorption-like configuration appears at near  $\sim 2.2$  Å along the physisorption branch. Black symbols mark the local minima on each branch.  $\Delta\Omega_{un}$  denotes the adsorption energy without ZPE, entropy, or thermal corrections. The graphene C atoms are colored gray, the  $CO_2$  C atoms purple, and the N, O, and Ni atoms blue, red, and cyan, respectively.

competitive state at  $-2.0$  V, and finally becoming the global minimum at  $-2.5$  V.

A notable feature arises at shorter C–Ni distances along the physisorption energy curve: a kink at  $-1.5$  and  $-2.0$  V that develops into a local minimum at  $-2.5$  V (solid circle). This feature corresponds to an alternative metastable chemisorption-like configuration ( $C_{2v}$ – $D_{2h}$ ), in which  $CO_2$  becomes partially activated while the Ni– $N_4$  unit remains essentially planar. Accordingly, at  $U = -2.5$  V, the physisorption branch contains two local minima: a shallow minimum near  $\sim 3$  Å, corresponding to a weakly bound, nearly linear  $CO_2$  state with negligible charge transfer, and a second minimum near  $\sim 2.2$  Å, where  $CO_2$  is bent and partially charge-transferred.

Together, these trends reveal the intrinsic potential dependence of  $CO_2$  adsorption: physisorption dominates at less negative potentials, while chemisorption becomes thermodynamically preferred as the potential is more negative.

To elucidate the nature of these three energy minima, we examined the net charge transfer to  $CO_2$  and their geometric characteristics (Figure 3b–d). Note that the net charge shown for  $CO_2$  in Figure 3b represents a local charge-partitioning result for the adsorbate and should not be confused with the global excess electron count  $N$  in the Landau free energy expression. The physisorption minimum at  $\sim 3$  Å exhibits negligible charge transfer, a linear  $CO_2$ , and a planar Ni– $N_4$  motif, consistent with a weakly bound  $D_{\infty h}$ – $D_{2h}$  configuration.

At  $U = -2.5$  V, a local minimum emerges along the physisorption curve at  $\sim 2.2$  Å, which shows moderate charge transfer and CO<sub>2</sub> bending while the Ni–N<sub>4</sub> unit remains essentially planar, indicating a C<sub>2v</sub>–D<sub>2h</sub> chemisorption mode. In contrast, the minimum along the chemisorption curve exhibits the largest charge transfer, significant CO<sub>2</sub> bending, and a distinct out-of-plane Ni displacement, characteristic of the C<sub>2v</sub>–C<sub>2v</sub> chemisorption mode.

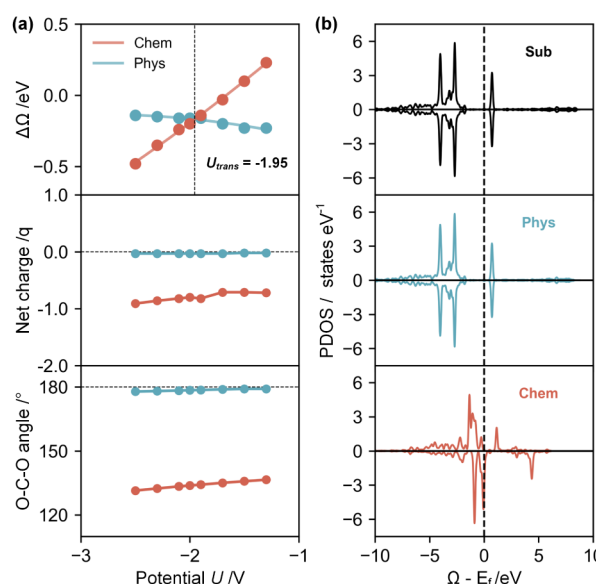
The enhanced stability of the C<sub>2v</sub>–C<sub>2v</sub> chemisorption mode arises from improved symmetry-allowed overlap and energy alignment between the CO<sub>2</sub> a<sub>1</sub> orbital and the Ni d<sub>z<sup>2</sup></sub> orbital (Figure 2b). In second-order perturbation theory, better energy alignment lowers the electronic energy and strengthens the chemisorption interaction. Although pyramidalization of the Ni–N<sub>4</sub> site incurs some strain penalty, the concurrent electronic stabilization due to stronger C–Ni interaction outweighs this cost, yielding a net thermodynamic gain for the CO<sub>2</sub>–Ni–N<sub>4</sub> system. In addition, electron donation from Ni into the a<sub>1</sub> orbital promotes additional bending, further reinforcing the chemisorption via a pseudo-Jahn–Teller effect.

To better understand how adsorption reshapes the CO<sub>2</sub> electronic structures, we analyzed the Walsh diagrams (shown in Figures S5–S7) that track the evolution of orbital energies as the molecule bends. Prior work by Wang et al. examined orbital splitting in isolated CO<sub>2</sub>,<sup>75</sup> whereas our analysis explicitly includes surface-molecule interactions and charge transfer. Among all the orbitals examined, only the a<sub>1</sub> orbital stabilizes (lowers in energy) upon bending, consistent with a reduction in nodal planes from 3 to 2. As CO<sub>2</sub> distortion increases, the degenerate  $\pi_u$  orbitals split into a higher-energy b<sub>1</sub> orbital and multiple lower-energy a<sub>1</sub>-derived states (Figures S8–S13). These a<sub>1</sub>-derived states appear exclusively in chemisorbed configurations and span the Fermi level, enabling electron donation into CO<sub>2</sub> that stabilizes adsorption.

Compared to the C<sub>2v</sub>–D<sub>2h</sub> chemisorption found along the physisorption curve, the C<sub>2v</sub>–C<sub>2v</sub> state on the chemisorption curve exhibits deeper a<sub>1</sub> orbital penetration and stronger stabilization, driven by symmetry reduction of the Ni–N<sub>4</sub> site. This pyramidal distortion shortens the C–Ni distances, enhances orbital overlap (Ni d<sub>z<sup>2</sup></sub> → CO<sub>2</sub> a<sub>1</sub>), strengthens CO<sub>2</sub> binding, and shifts the global minimum toward chemisorption at more negative potentials, highlighting the critical role of symmetry breaking in CO<sub>2</sub> activation.

To quantify the potential-dependent crossover in CO<sub>2</sub> adsorption modes, we define the “transorption” potential ( $U_{\text{trans}}$ ) as the applied potential at which the thermodynamic minimum switches from physisorption to chemisorption (C<sub>2v</sub>–C<sub>2v</sub>). For Ni–N<sub>4</sub>, the physisorption minimum is essentially potential-invariant in Landau free energy ( $\Delta\Omega$ ), net charge transfer ( $\approx 0$ ), and O–C–O angle (near-linear), whereas the chemisorption minimum shows a strong potential dependence:  $\Delta\Omega$  decreases (stabilizes) with more negative  $U$ , the magnitude of electron transfer to CO<sub>2</sub> increases, and the O–C–O angle progressively decreases (greater bending), crossing the physisorption minimum at  $U_{\text{trans}} = -1.95$  V (Figure 4a). The electron transfer and bond angle characteristics distinguish the two modes and verify the transition. Consistently, the projected density of states (PDOS) analysis reveals substantial electronic restructuring at the Ni center upon chemisorption compared to the pristine surface and physisorption state (Figure 4b).

With the Ni–N<sub>4</sub> case established, we then explored whether this crossover holds true across the 3d TM–N<sub>4</sub> SACs.



**Figure 4.** (a) Potential-dependent Landau adsorption free energies ( $\Delta\Omega$ ), net charge transfer ( $q$ ), and O–C–O bond angle for the minimum-energy states on the physisorption (blue) and chemisorption (red) curves of Ni–N<sub>4</sub>. The vertical dashed line marks the transorption potential  $U_{\text{trans}} = -1.95$  V. (b) Partial density of states (PDOS) of the Ni active center for the pristine substrate (Sub), physisorbed (Phys), and chemisorbed (Chem) states at  $U_{\text{trans}}$  referenced to the Fermi level ( $E_F$ ). Corresponding results for the other nine TMs are given in Figures S14–S22.

Surveying all 3d TM–N<sub>4</sub> SACs (Figures S14–S22) reveals analogous profiles, in which the physisorption minimum is weakly potential dependent, whereas the chemisorption minimum stabilizes with increasing overpotential, yielding a well-defined  $U_{\text{trans}}$  for each metal (the corresponding values are summarized in Table S9).

To assess whether the concept of  $U_{\text{trans}}$  can be extended beyond TM–N<sub>4</sub> SACs, we applied the same constant-potential framework to the dropping Hg electrode. Notably, applying the same calculation framework to a Hg slab yields a crossover potential of  $U_{\text{trans}} = -1.89$  V (Figure S23a–b and Table S10), consistent with the experimental value inferred from polarographic measurements (see Part 1 of the Supporting Information), where CO<sub>2</sub><sup>•−</sup> formation is observed at  $-1.98$  V vs SHE.<sup>76–78</sup> At this potential, CO<sub>2</sub> adopts a bent geometry in the chemisorbed state (Figure S23c), consistent with prior reviews of adsorbed CO<sub>2</sub>.<sup>79,80</sup> The bent geometry closely resembles that of the solvated CO<sub>2</sub><sup>•−</sup>,<sup>78,81</sup> as also reproduced in our calculations (Figure S23d).

Therefore, the CO<sub>2</sub> adsorption-mode transition emerges as a recurring, potential-dependent feature across the systems examined here; for TM–N<sub>4</sub> SACs, it is governed by symmetry lowering and electronic reorganization at sufficiently negative potentials. At the same time, any extension of this concept to broader catalyst families or other electrocatalytic reactions should be regarded as a promising future direction rather than an established conclusion of the present work.

### Machine-Learning Analysis

ML provides a data-driven approach to uncovering complex structure–property relationships and identifying key descriptors that may be overlooked in conventional analyses.<sup>82–85</sup> To probe the factors governing the CO<sub>2</sub> adsorption-mode crossover across 3d TM–N<sub>4</sub> SACs, we employed the SISSO

method<sup>74</sup> to isolate the key parameters influencing  $U_{\text{trans}}$ . We emphasize that SISSO is used here not as a predictive model for unexplored catalysts, but as a data-driven tool to validate and rationalize the orbital-level mechanisms governing CO<sub>2</sub> chemisorption identified in the previous section. To this end, we selected 21 features (Table 1): 8 atomic descriptors of the

**Table 1. Features Used for Machine Learning**

|                | Feature                                                | Symbol (formula)                     | Label (plot)                     |
|----------------|--------------------------------------------------------|--------------------------------------|----------------------------------|
| Atomic (TMs)   | Electronegativity <sup>a</sup>                         | $EN$                                 | $F_1$                            |
|                | First ionization energy (eV) <sup>a</sup>              | $El_a$                               | $F_2$                            |
|                | Binding energy of metal dimers (eV) <sup>b</sup>       | $Eb_a$                               | $F_3$                            |
|                | Electron numbers in s and d orbitals <sup>a</sup>      | $N_{s+d}$                            | $F_4$                            |
|                | s and d orbital radii (Å) <sup>a</sup>                 | $R_s, R_d$                           | $F_5, F_6$                       |
|                | Atomic radius (Å) <sup>c</sup>                         | $R_a$                                | $F_7$                            |
| Bulk (TMs)     | Mass (g/mol) <sup>c</sup>                              | $M$                                  | $F_8$                            |
|                | Cohesive energy (eV) <sup>b</sup>                      | $E_{coh}$                            | $F_9$                            |
|                | Energies of d-band center (eV) <sup>a</sup>            | $E_{db}$                             | $F_{10}$                         |
| Surface (SACs) | Energies of $d_{x^2-y^2}$ , $d_{z^2}$ , $d_{xy}$       | $E_{x^2-y^2_s}, E_{z^2_s}, E_{xy_s}$ | $F_{11}, F_{12}, F_{13}, F_{14}$ |
|                | $d_{xz}$ - and $d_{yz}$ -band center (eV) <sup>a</sup> | $E_{xz_s}, E_{yz_s}$                 | $F_{15}, F_{16}$                 |
|                | Fermi level (eV) <sup>a</sup>                          | $E_{F_s}$                            | $F_{17}$                         |
|                | Electron numbers in different orbitals <sup>a</sup>    | $N_{x^2-y^2_s}, N_{z^2_s}$           | $F_{18}, F_{19}$                 |
|                |                                                        | $N_{xy_s}, N_{xz_s}, N_{yz_s}$       | $F_{20}, F_{21}$                 |

<sup>a</sup>Electronic structures. <sup>b</sup>Structure stabilities. <sup>c</sup>Physical properties.

transition metals (Atomic (TMs)), 2 bulk metal properties (Bulk (TMs)), and 11 surface descriptors of the SACs (Surface (SACs)). The atomic and bulk features were obtained from the consistently generated data set of Han et al.,<sup>86</sup> whereas the surface descriptors were calculated in this work. These features

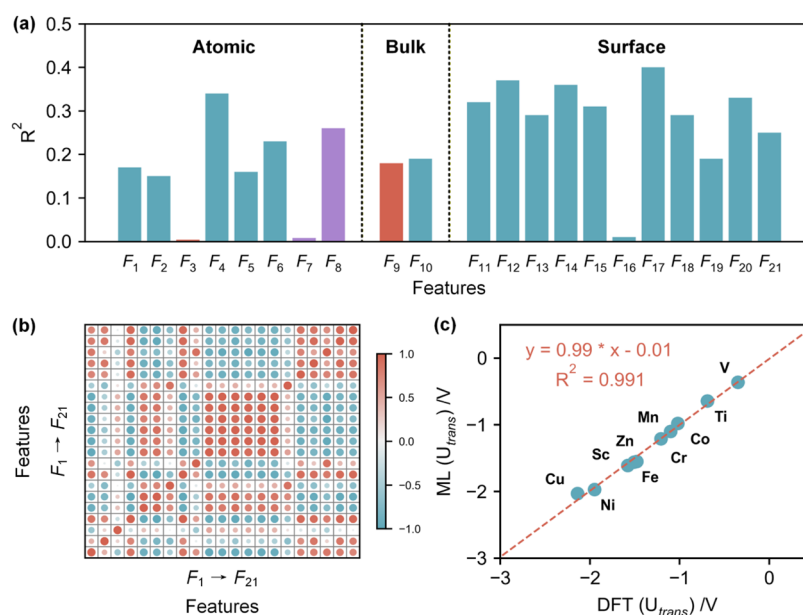
can be further categorized as 17 electronic structures, 2 structural stabilities, and 2 general physical properties.

To assess whether  $U_{\text{trans}}$  can be captured by a single variable, we first examined its linear correlations with each feature. The resulting  $R^2$  values (Figure 5a) are uniformly low (0.004–0.39), and the pairwise plots (Figures S24–S48) show weak or highly dispersed trends. Thus, no single descriptor suffices to explain  $U_{\text{trans}}$ , and a multifeatured model is required to capture the adsorption-mode crossover. Having established the need for a multifeatured model, we next assessed interdependencies among descriptors. We employed the Pearson correlation matrices (Figure 5b) to visualize pairwise relationships among the features. As expected, when treating individual  $d$  orbitals as separate descriptors, strong multicollinearity is observed among the orbital-resolved  $d$ -band centers ( $E_{x^2-y^2_s}, E_{z^2_s}, E_{xy_s}, E_{xz_s}, E_{yz_s}$ ) and corresponding occupancies ( $N_{x^2-y^2_s}, N_{z^2_s}, N_{xy_s}, N_{xz_s}, N_{yz_s}$ ). This correlation reflects their collective participation in TM–CO<sub>2</sub> bonding. Although correlated, these orbitals contribute through distinct symmetry channels and therefore retain independent mechanistic significance, enabling the differentiation between  $\sigma$ -donation and  $\pi$ -back-donation contributions. Notably, several of these features also emerged as critical in our symmetry/Walsh analysis of adsorption-mode transition. Therefore, keeping these correlated features enhances the interpretability of our ML model and preserves sensitivity to the distinct bonding channels that govern CO<sub>2</sub> chemisorption.

To construct a compact and physically interpretable model for  $U_{\text{trans}}$ , we examined SISSO models with increasing dimensionality. The resulting 1D SISSO model is given by

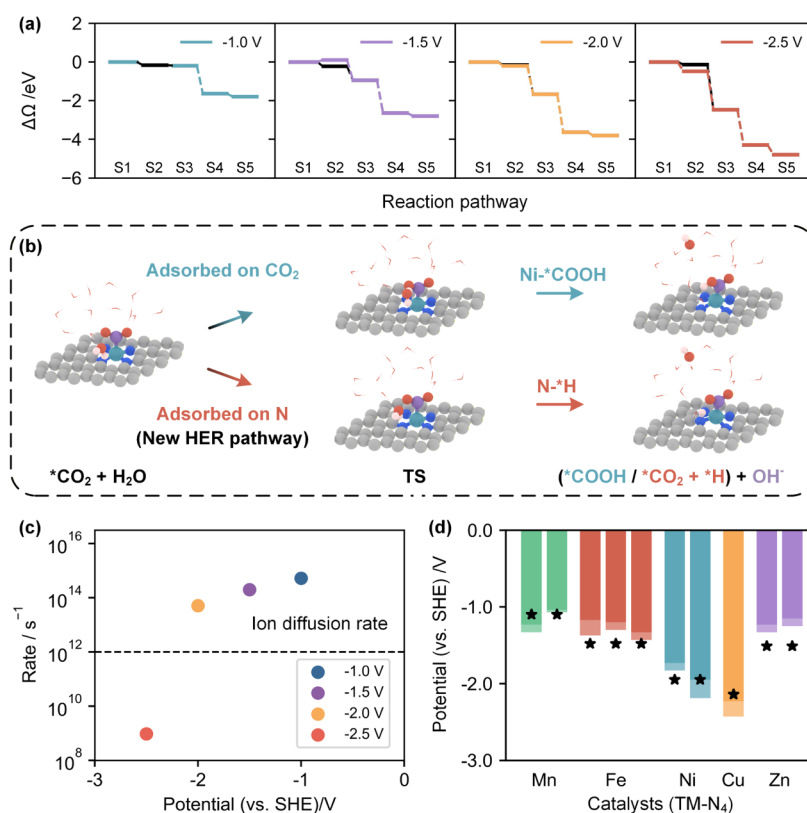
$$U_{\text{trans}} = -0.48 \times \ln(|E_{db} - E_{x^2-y^2_s}| - |E_{yz_s} - E_{z^2_s}|) - 1.58 \quad (6)$$

which combines three surface electronic features and one bulk descriptor. The 2D SISSO model is summarized in Table S11.



**Figure 5.** (a) Summary of  $R^2$  values corresponding to the correlations between  $U_{\text{trans}}$  and each feature. The features of electronic structures, structure stabilities, and physical properties are colored in blue, red, and purple, respectively. (b) Pearson correlations between the selected 21 features. (c) The  $U_{\text{trans}}$  comparison between the results from the ML simulations and DFT calculations.





**Figure 6.** (a) Landau free energy diagram for CO<sub>2</sub>RR on Ni–N<sub>4</sub> SAC under applied potentials of  $U = -1.0, -1.5, -2.0,$  and  $-2.5$  V vs SHE. The reaction states are denoted as S1–S5, corresponding to S1 =  $*+CO_2$ , S2 =  $*CO_2$ , S3 =  $*COOH$ , S4 =  $*CO$ , and S5 =  $* + CO$ . The physisorption branch is shown in black, whereas the CO<sub>2</sub> chemisorption branch is shown in the color corresponding to each applied potential; at  $U = -1.0$  V, only physisorption is accessible. (b) Competing hydrogenation pathways on Ni–N<sub>4</sub> SAC following CO<sub>2</sub> chemisorption:  $*COOH$  formation versus a coordinating-N-mediated HER pathway. The aqueous environment is represented by stick models, while the reaction intermediates are highlighted using ball-and-stick models. (c) Calculated electron-hopping rates at different applied potentials; the dashed line denotes the estimated ion-diffusion rate. (d) Calculated  $U_{trans}$  values (asterisks) versus experimental onset potential for CO yield decline (bars) across various TM–N<sub>4</sub> SACs (M = Mn, Fe, Ni, Cu, and Zn). The lighter bars denote the experimental potential intervals after conversion to the SHE scale. This catalyst-by-catalyst representation complements the parity-style comparison shown in the Figure 1 inset, and the dedicated parity plot is shown in Figure S56.

The 1D model correlates strongly with the DFT-computed  $U_{trans}$ , achieving an  $R^2$  value of 0.991 (Figure 5c), whereas the 2D model improves the fit only marginally ( $R^2 = 0.992$ ) at the cost of substantially greater complexity.

To evaluate the robustness and possible overfitting, we performed LOOCV for both 1D and 2D SISSO models. The resulting expressions for each fold are listed in Tables S12–S13, and the corresponding held-out predictions are summarized in Table S14. For the 1D model, 9 out of 10 folds recover the same four primary descriptors identified in the full-data fit, while the remaining fold yields a closely related expression that still retains two of those four descriptors. This strong recurrence indicates that the 1D descriptors are robust and not controlled by any single data point. By contrast, the 2D SISSO model exhibits notable fold-to-fold variability in the second component, reflecting increased sensitivity to data perturbation and hence lower robustness. The held-out predictions further demonstrate a clear difference in cross-validated performance: the 1D model yields LOOCV MAE, RMSE, and  $R^2$  values of 0.090 V, 0.136 V, and 0.95, respectively, whereas the corresponding errors for the 2D model deteriorate substantially to 0.520 V, 0.828 V, and 0.23. Thus, the 2D model shows poorer held-out predictive performance and lower descriptor stability. Collectively, these

results support the 1D SISSO model as the more robust and interpretable framework adopted in this work.

To quantify the relative importance of each component in the 1D SISSO model, we performed an ablation study, in which each primary descriptor was individually replaced by its data set-averaged value, and the resulting increase in prediction mean square error was used to estimate its contribution. The relative contributions are 31.75%, 26.96%, 24.51%, and 16.78% for  $E_{x^2-y^2}$ ,  $E_{yz}$ ,  $E_{z^2}$ , and  $E_{d_{xy}}$ , respectively. Thus, the surface electronic descriptors dominate the model performance, together accounting for more than 80% of the total contribution.

With the 1D model established, we next examine the physical origin of the main descriptors in the CO<sub>2</sub> adsorption process. During chemisorption, the CO<sub>2</sub> molecule transforms from linear  $D_{\infty h}$  to bent  $C_{2v}$ , reorganizing its frontier molecular orbitals (Figure 2b). The originally degenerate  $\pi_u$  and  $\pi_g$  sets split into ( $b_1$  and  $a_1$ ) and ( $b_2$  and  $a_2$ ), respectively. Based on symmetry considerations, four symmetry-allowed metal–ligand couplings are found: (1) CO<sub>2</sub>- $b_1$  with Ni- $b_1$  in  $C_{2v}$  ( $d_{xz}$ ) and with Ni- $b_{2g}$  in  $D_{2h}$ , (2) CO<sub>2</sub>- $a_1$  with Ni- $a_1$  in  $C_{2v}$  ( $d_{z^2}$  or  $d_{x^2-y^2}$ ) and with Ni- $a_g$  in  $D_{2h}$ , (3) CO<sub>2</sub>- $a_2$  with Ni- $a_2$  in  $C_{2v}$  ( $d_{xy}$ ) and with Ni- $b_{1g}$  in  $D_{2h}$ , and (4) CO<sub>2</sub>- $b_2$  with Ni- $b_2$  in  $C_{2v}$



( $d_{yz}$ ) and with  $Ni-b_{3g}$  in  $D_{2h}$ . Consistent with the ML analysis, the  $Ni\ d_{yz}$ ,  $d_{z^2}$ , and  $d_{x^2-y^2}$  orbitals contribute most significantly to the  $CO_2$  chemisorption, because they engage most strongly with the bent  $CO_2-a_1$  (new LUMO) and  $b_2$  (new HOMO) states. Thus,  $CO_2$  binding is governed by  $HOMO \rightarrow$  metal donation ( $CO_2-b_2$ , lone electron pair to  $Ni\ d_{yz}$ ) and metal  $\rightarrow$  LUMO back-donation ( $Ni\ d_{z^2}$  or  $d_{x^2-y^2}$  into  $CO_2-a_1$ ), in line with the observed charge-transfer trends and orbital-energy alignment.

Interestingly, although the bent- $CO_2-a_1$  derives from the linear  $\pi_u$  set, its interaction with  $Ni-d_{z^2}$  is predominantly  $\sigma$ -bonding, with no nodal plane along the  $Ni-C$  axis. This interaction presents an unusual  $\sigma$  back-donation, in which electron density flows from  $Ni\ d_{z^2}$  into the  $CO_2-a_1$  acceptor. The charge transfer map (Figure 3b) and Walsh diagram (Figures S5–S7) both corroborate electron injection into the  $a_1$  orbital upon chemisorption. This  $\sigma$  back-donation motif echoes bonding patterns in TM-ligand complexes,<sup>87–90</sup> but here is enabled by symmetry lowering of the  $Ni-N_4$  site from  $D_{2h}$  to  $C_{2v}$ , which shortens the  $Ni-C$  distance and enhances the overlap between  $CO_2-a_1$  and  $Ni-d_{z^2}$  orbitals. The resulting stronger coupling increases orbital splitting and charge transfer, ultimately promoting  $CO_2$  activation and stabilizing the chemisorbed state. Therefore, the consistency among the electronic structure analysis, the symmetry/Walsh picture, and the SISSO model underscores the critical role of TM  $d$ -orbitals in stabilizing  $CO_2$  chemisorption.

### $CO_2RR$ Processes Based on FCP Computations

In this section, we analyze  $CO_2$ -reduction processes on  $Ni-N_4$  SAC. The Landau free energy diagrams at selected potentials are shown in Figure 6a, with chemisorption and physisorption states distinguished by colored and black lines, respectively, and the complete reaction pathway is illustrated in Figure S49. Because each free-energy profile in Figure 6a was obtained self-consistently at its own applied potential, the differences between the profiles do not arise from a simple rigid shift by the potential difference; rather, they reflect the potential-dependent electron transfer with each intermediate and scale approximately with  $-\Delta N_e \Delta U$  when two potentials are compared.

Across potentials, the free-energy profile is generally exergonic, except for the route involving  $CO_2$  chemisorption at  $U = -1.5$  V. Notably, at  $U = -1.0$  V, only physisorption occurs, as chemisorption is not observed at this less negative potential. At  $U = -1.5$  V,  $CO_2$  chemisorption becomes reachable but remains less stable than physisorption. At  $U = -2.0$  V, close to the computed  $U_{trans} = -1.95$  V, chemisorption slightly surpasses physisorption (Figure 4a), and at  $U = -2.5$  V, it becomes clearly dominant. Therefore,  $CO_2RR$  proceeds primarily via a physisorption-dominated pathway (with CEPT mechanism) at less negative potentials, and transitions to a chemisorption-dominated pathway (with DEPT mechanism) once the applied potential is more negative than  $U_{trans}$ .

To quantify how applied potential reshapes the  $CO_2RR$  mechanism, we tracked the transition of the RLS, the elementary step with the largest free-energy span  $\Delta\Omega$  per the Bell–Evans–Polanyi principle.<sup>91,92</sup> As shown in Figure 6a, at  $-1.0$  V, the RLS is  $^*COOH$  formation on the physisorption pathway (black segment at the second step; chemisorption is absent at this potential), whereas upon driving the potential more negative, the  $CO$  release free-energy span surpasses that

of  $^*COOH$  formation, resulting in the RLS shift between  $-1.0$  and  $-1.5$  V. Beyond this transition, at more negative potentials of  $-2.0$  to  $-2.5$  V, the energy differences for most steps decrease; however, the  $CO$  release span consistently maintains the largest and thus the RLS. Notably, the  $CO$  release free-energy change is nearly constant at  $U = -1.0$ ,  $-1.5$ , and  $-2.0$  V, then drops at  $-2.5$  V, foreshadowing  $CO$  production change at the most reducing potentials.

We next examine how these RLS transitions relate to the  $CO$  yield behavior depicted in Figure 1. At potentials less negative than  $-1.0$  V, prior CP studies showed that the  $^*COOH$  step is endergonic but progressively stabilizes as the potential becomes more negative,<sup>38,43</sup> consistent with its role as the RLS and with the experimentally observed initial rise in  $CO$  yield.<sup>93–95</sup> At  $-1.0$  V, the RLS is  $^*COOH$  formation on the physisorption pathway (black segment at the second step; chemisorption is absent at this potential). As the potential becomes more negative, the free-energy span for  $CO$  release surpasses that of  $^*COOH$  formation, resulting in an RLS shift between  $-1.0$  and  $-1.5$  V. Once  $CO$  release becomes rate-limiting, its free-energy span remains nearly unchanged up to  $-2.0$  V. Within the Bell–Evans–Polanyi framework, this corresponds to a nearly constant kinetic bottleneck, which naturally gives rise to the experimentally observed plateau in  $CO$  yield.<sup>23,31</sup> Beyond  $-2.0$  V, the production plateau terminates as the  $CO$ -release free energy span changes and additional factors, including HER onset at N sites and slower electron-transfer, begin to depress activity, leading to the eventual decline in  $CO$  yield. Taken together, these mechanistic elements reproduce the  $CO$  yield trend observed experimentally, including the initial rise, the intermediate plateau, and the eventual decline (Figures 1 and S1).

To rationalize the experimentally observed postplateau decline in  $CO$  yield, we first note that its onset potential closely coincides with  $U_{trans}$  (Figure S1), where  $CO_2$  adsorption on  $Ni-N_4$  SAC shifts from physisorption to chemisorption. This correspondence suggests a mechanistic link, inspiring us to propose a new HER pathway at more negative potentials: the coordinated N atoms may become active for HER once  $CO_2$  chemisorbs, introducing a competing pathway that consumes protons and electrons (Figure 6b) and thereby suppresses  $CO$  production. To probe this possibility, we computed the reaction profiles for the first branching hydrogenation after  $CO_2$  adsorption, specifically,  $^*COOH$  formation and competing  $^*H$  adsorption on one of the four coordinating N sites, namely,  $Ni-N_4$  SAC, at  $U_{trans}$  using the CI-NEB method (Figure S50), and incorporated the resulting activation barriers and energetics into microkinetic selectivity analyses (Figure S51). At  $U_{trans}$ , the  $^*COOH$  formation and competing N-site H adsorption have comparable activation barriers of 0.17 and 0.20 eV, respectively; because  $^*COOH$  formation remains thermodynamically more favorable, the N-site HER pathway is kinetically accessible but not dominant under these conditions. These representative steps were selected because the first hydrogenation step determines whether the reaction branch proceeds toward  $CO_2RR$  or HER at  $U_{trans}$ . The preliminary trends agree well with experiment, supporting the plausibility of the N-site HER pathway. Nevertheless, these microkinetic results should be viewed as preliminary mechanistic insights rather than a complete treatment of the reaction environment. A more comprehensive constant-potential DFT study, ideally combined with targeted experiments, will be needed to further

validate this hypothesis. In addition, coupling microkinetic simulations with a continuum transport model will be essential for rigorously assessing hydrodynamic diffusion and other transport effects.

Notably, this unique potential-dependent, CO<sub>2</sub>-chemisorption-triggered HER mechanism proposed here differs fundamentally from conventional N-doping strategies for HER, where N primarily modulates the electronic structure of adjacent metal<sup>96–98</sup> or carbon<sup>99</sup> sites without serving as the direct H-adsorption center. In contrast, our results indicate that the coordinating N atom itself is an active site for HER once CO<sub>2</sub> is chemisorbed at the Ni–N<sub>4</sub> site, diverting protons/electrons and suppressing CO formation. In addition, Boppella et al. recently demonstrated experimentally that N atoms proximal to the catalytic TM center can participate in H adsorption,<sup>100</sup> providing direct evidence that nearby N motifs can serve as proton-binding sites. This observation supports the mechanistic relevance of our prediction, suggesting that the N atoms surrounding Ni–N<sub>4</sub> may indeed act as additional HER-active sites under CO<sub>2</sub>RR conditions.

Beyond thermodynamics, we examined electron transfer (ET) as a second factor that can affect CO yield, particularly at strongly negative potentials. We evaluated the electron hopping rate between the adsorbate and Ni–N<sub>4</sub> using the method proposed by Nørskov, Strasser, Chan, and coworkers,<sup>16,101</sup> which was originally formulated for chemisorbed species with an adsorbate PDOS peak at the Fermi level. Here, we generalize this approach to systems where the adsorbate PDOS peak is offset from  $E_f$  or the adsorbate has a finite band gap, thereby enabling its application to adsorbates with metallic or semiconducting behavior (derivation provided in [Part 2 of the Supporting Information](#)). Since CO<sub>2</sub> prefers physisorption at less negative potentials, we selected \*COOH, a chemisorbed intermediate, as the probe species. The half-width ( $\Delta$ ) was obtained from the \*COOH PDOS near  $E_f$  ([Figures S52–S55](#)), and the corresponding DOS height was normalized to the maximum DOS at the same energy across comparison cases. The ET rate was then estimated using Fermi's Golden Rule (for details, please refer to [Part 2 of the Supporting Information](#)).

To assess whether ET limits activity at high overpotentials, we quantified ET rates versus applied potentials. [Figure 6c](#) summarizes ET rates, in which the dashed line represents the estimated ion diffusion rates proposed by Nørskov's group on the Pt(111) facet and Fe–N<sub>4</sub> SAC.<sup>16,102</sup> From  $-1.0$  to  $-2.0$  V, ET rates exceed the ion diffusion rate by roughly 2 orders of magnitude, indicating that ET is not rate-limiting at modest overpotentials. In contrast, between  $-2.0$  and  $-2.5$  V, the ET rate drops sharply and falls below the ion diffusion benchmark, suggesting that ET may contribute to the decline in CO production. This observation aligns with experimental findings, where the CO yield significantly decreases at more negative potentials following a production plateau.<sup>23,31</sup> Thus, while ET does not hinder CO<sub>2</sub> reduction performance at mild potentials, it can contribute to the observed decline in CO yield under strongly reducing conditions.

Building on the finding that the  $U_{\text{trans}}$  coincides with the experimentally observed onset of CO yield decline on Ni–N<sub>4</sub> SAC, we further examined whether this correlation between computations and experiments holds across 3d series. [Figure 6d](#) compares five TM–N<sub>4</sub> SACs (TM = Mn, Fe, Ni, Cu, and Zn): experimental decline potentials are shown as bars,<sup>23,31,103–110</sup> while computational  $U_{\text{trans}}$  data appear as

asterisks. To facilitate direct comparison between experiment and theory across catalysts, we present the computed  $U_{\text{trans}}$  values and the experimentally observed onset potentials for CO-yield decline side by side in [Figure 6d](#). This catalyst-by-catalyst representation makes the agreement in both absolute range and relative ordering more transparent. For a complementary global view, the corresponding parity-style comparison is also shown in the inset of [Figure 1](#), and the dedicated parity plot is shown in [Figure S56](#). The experimental data sets for each element are detailed in [Figures S1](#) (Ni) and [S57](#) (Mn, Fe, Cu, Zn). To reflect the discrete potential steps used in the experiments, we employ a lighter color range in the diagram to indicate the measurement step size and the associated uncertainty. The exact optimal potential in experiments remains unknown, but is expected to fall within these intervals. It should be noted that, although the experimental catalysts are generally assigned to TM–N<sub>4</sub> motifs, their local coordination environments may deviate from the idealized TM–N<sub>4</sub> structures considered in our calculations. Moreover, the experimental data were collected from catalysts prepared and evaluated under different conditions. Recent round-robin testing has shown that appreciable variability in catalytic performance can persist even when identical catalyst batches and standardized testing protocols are used across laboratories, highlighting the uncertainty associated with cross-study comparisons of literature-derived experimental data.<sup>111</sup> Accordingly, the comparisons in [Figures 6d](#) and [S56](#) are intended as a semiquantitative cross-catalyst assessment rather than a strict one-to-one comparison among structurally identical TM–N<sub>4</sub> sites.

Within these limitations, the computed  $U_{\text{trans}}$  trend, Mn < Zn < Fe < Ni < Cu, well matches the experimental findings, which highlights the critical role of CO<sub>2</sub> chemisorption and supports  $U_{\text{trans}}$  as a reliable parameter for predicting CO production trends across TM–N<sub>4</sub> catalysts. We note that previous studies have explored geometry-based descriptors for CO<sub>2</sub> activation and catalytic performance, focusing on structural features such as bond elongation and bending on metal<sup>112</sup> and metal oxide surfaces.<sup>113</sup> In contrast, our work introduces  $U_{\text{trans}}$  as a potential-based descriptor, providing an alternative approach with experimentally measurable quantities.

In addition to the correlation between  $U_{\text{trans}}$  and CO yield decline, the free energy diagram revealed another agreement with experiments. Specifically, only Fe– and Cu–N<sub>4</sub> SACs exhibit an endergonic CO release process ([Figures S58 and S59](#)), whereas the other three TM–N<sub>4</sub> SACs (Mn, Ni, and Zn) show exergonic CO release ([Figures S60 and S61](#)). Since CO is a key precursor for C<sub>2</sub> product formation, strong CO binding on Fe– and Cu–N<sub>4</sub> SACs may inhibit CO desorption, favoring CO poisoning while simultaneously promoting the formation of C<sub>2</sub> products. Notably, our results align well with the experimentally observed CO poisoning on Fe–N<sub>4</sub> SAC<sup>114</sup> and the presence of C<sub>2</sub> products on Cu–N<sub>4</sub> catalysts.<sup>108,115</sup> In contrast, CO remains the primary product for Mn–,<sup>103,116</sup> Ni–,<sup>27,30</sup> and Zn–N<sub>4</sub> SACs,<sup>109,117,118</sup> consistent with their weaker CO binding and facile desorption.

To evaluate the thermal stability of key intermediates, we performed fixed-electron-number AIMD simulations across the five TM–N<sub>4</sub> SACs using electron numbers initialized from the corresponding CP-DFT calculations at  $U_{\text{trans}}$ . The energy evolution profiles and C–TM distances of the adsorbed intermediates are presented in [Figures S62–S71](#). Despite

thermal fluctuations in orientations and C–TM separation during the simulations, chemisorbed  $^*\text{CO}_2$  remained stably bound on all systems, confirming the viability of the chemisorption mode at  $U_{\text{trans}}$  and supporting a mechanistic shift from CEPT to DEPT. In contrast, CO exhibits metal-dependent behavior: spontaneous desorption events appear on Mn–, Ni–, and Zn– $\text{N}_4$  SACs, whereas CO remains persistently adsorbed on Cu– and Fe– $\text{N}_4$  SACs. These findings are consistent with our previous thermodynamic analysis (endergonic CO release on Fe/Cu) and align well with experimental observations, where Fe– $\text{N}_4$  SAC tends to suffer from CO poisoning, while Cu– $\text{N}_4$  SAC presents good performance for  $\text{C}_2$  product formation.

To delineate the scope, we restricted cross-metal comparisons to five representative TM– $\text{N}_4$  SACs. Although Co– $\text{N}_4$  has been studied experimentally, we did not include it here because of its  $\text{CO}_2\text{RR}$  performance is markedly inferior to Ni– $\text{N}_4$ .<sup>21,22,119</sup> Moreover, while Co-based molecular complexes have shown promising  $\text{CO}_2$  reduction activity,<sup>120</sup> their architectures differ fundamentally from graphene-anchored SACs: they lack a robust carbon matrix as a secondary coordination shell, and their coordinating N atoms are embedded within the 5-membered carbon rings rather than a graphene lattice. Consequently, performance data from Co-containing molecular systems are not directly transferable to the TM– $\text{N}_4$  models investigated in this work.

Recent constant-potential studies have highlighted that the electronic configuration of the metal center can evolve under bias. In particular, Cui et al. examined  $\text{CO}_2\text{RR}$ –HER competition on Ni– $\text{N}_4$  under an OH-ligated Ni assumption, mapping Faradaic-efficiency (FE) changes over  $-0.4$  to  $-0.9$  V (vs RHE).<sup>46</sup> Their study highlights ligand effects at the Ni center and a potential-induced hybridization-state transition of Ni– $\text{N}_4$  (from an inert  $\text{dsp}^2$  to an active  $\text{d}^2\text{sp}^3$  configuration), and stands among the earliest CP works to directly simulate FE diagrams to rationalize CO– $\text{H}_2$  selectivity. Our work is complementary and adsorbate-centric: with the CP framework, we uncover a potential-driven transition of  $\text{CO}_2$  adsorption modes that sets the onset of Ni-site occupation by chemisorbed  $\text{CO}_2$  and predicts the decline of CO partial current density beyond  $U_{\text{trans}}$ . This crossover naturally activates neighboring N atoms as HER sites, providing a mechanistic route for  $\text{CO}_2\text{RR}$ –HER competition at high overpotentials. Thus, while Cui et al. rationalize selectivity via Ni-center hybridization and ligand effects, we explain the full PCD evolution (rise  $\rightarrow$  plateau  $\rightarrow$  decline) via adsorption-state switching and its kinetic consequences. Together, these two views offer orthogonal, mutually reinforcing levers for understanding and optimizing TM– $\text{N}_4$  SACs under working conditions.

Recent experimental studies have expanded the description of SACs beyond the local TM– $\text{N}_4$  motif, highlighting the importance of both extended electronic interactions and potential-induced structural evolution. Wang et al. showed that long-range  $\pi$ -electron delocalization beyond the second coordination shell can substantially influence the electronic structure of the Ni center and stabilize the key  $^*\text{COOH}$  intermediate.<sup>121</sup> Shen et al. further demonstrated that an initially defined  $\text{CuN}_4$  site can undergo electrochemically induced coordination reconstruction to a self-healed  $\text{CuN}_1\text{O}_2$  configuration under working conditions.<sup>122</sup> These findings emphasize that experimentally relevant SAC active sites may involve electronic and structural degrees of freedom that are

not captured by an idealized local TM– $\text{N}_4$  model. Accordingly, because the present work focuses on idealized graphene-based TM– $\text{N}_4$  structures, the calculated  $U_{\text{trans}}$  values are not expected to be directly and quantitatively transferable to such more complex environments. Nevertheless, the physical concept underlying  $U_{\text{trans}}$  could be tested in these systems by explicitly incorporating their extended electronic environments and operando coordination structures into constant-potential calculations. Such extensions may provide a useful route toward connecting potential-dependent adsorption-state transitions with realistic catalyst structures and experimentally observed catalytic behavior.

## CONCLUSION

In summary, we employed the fully converged constant-potential method to investigate the potential-dependent transition of  $\text{CO}_2$  adsorption mode across ten 3d TM– $\text{N}_4$  SACs, with detailed analysis for Ni– $\text{N}_4$  and extensions to Mn, Fe, Ni, Cu, and Zn where experimental benchmarks exist. Landau free energy profiles exhibit three  $\text{CO}_2$  adsorption modes, including one physisorption ( $D_{\infty h}$ – $D_{2h}$ ) and two chemisorption ( $\text{C}_{2v}$ – $D_{2h}$  and  $\text{C}_{2v}$ – $\text{C}_{2v}$ ) states. Walsh diagrams and ML analyses indicate that increasingly negative potential stabilizes  $\text{CO}_2$  chemisorption by enhancing the  $\sigma$ -type back-donation and shortening the C–TM distances via symmetry lowering at the TM– $\text{N}_4$  center.

We further introduced the concept of the “transorption” potential ( $U_{\text{trans}}$ ), defined as the threshold potential at which chemisorption becomes thermodynamically preferred over physisorption, and used it to map CO yield evolution on Ni– $\text{N}_4$  SAC across three regimes: (1) At low overpotentials,  $\text{CO}_2$  is physisorbed and  $^*\text{COOH}$  formation is the RLS and its progressive stabilization with increasing overpotential accounts for the initial rise in CO yield; (2) At moderate overpotentials,  $\text{CO}_2$  still prefers physisorption thermodynamically, but the RLS shifts to CO desorption with a nearly potential-invariant span, giving a CO yield plateau; (3) Beyond  $U_{\text{trans}}$ ,  $\text{CO}_2$  prefers chemisorption, which activates N-site for HER and reduces electron transfer rates, jointly suppressing the CO yield.

By integrating constant-potential thermodynamics, orbital-symmetry reasoning, machine learning, and microkinetics, this work establishes  $U_{\text{trans}}$  as a predictive, DFT-derived descriptor that bridges computational and experimental investigation of TM– $\text{N}_4$  SACs. Critically, the framework quantitatively rationalizes the experimentally measured CO yield trend, capturing the rise-plateau-decline behavior and pinpointing the onset of the drop at  $U_{\text{trans}}$ . Practically,  $U_{\text{trans}}$  provides a screenable operating handle to maximize CO production while anticipating selectivity losses. Conceptually, the  $\sigma$ -back-donation/symmetry-lowering paradigm offers general design principles for activating linear molecules on atomically dispersed sites. Looking forward, integrating  $U_{\text{trans}}$  into ML/AI pipelines may offer a promising route for high-throughput, bias-aware screening of SACs and may inspire future exploration of related electrocatalytic transformations beyond  $\text{CO}_2\text{RR}$ .

## ASSOCIATED CONTENT

### Supporting Information

The Supporting Information is available free of charge at <https://pubs.acs.org/doi/10.1021/jacs.6c13568>.

Experimental data set of partial current density as a function of applied potential on Ni– $\text{N}_4$  SAC; structure



model of TM–N<sub>4</sub> SACs; assessment of the fixed-electron-number AIMD treatment; four possible CO<sub>2</sub> chemisorption configurations; CO<sub>2</sub> Walsh diagram at  $U = -1.5$ ,  $-2.0$ , and  $-2.5$  V vs SHE on Ni–N<sub>4</sub> SAC; Walsh diagram with corresponding PDOS of CO<sub>2</sub> along the chemisorption and physisorption curves at  $U = -1.5$ ,  $-2.0$ , and  $-2.5$  V vs SHE on Ni–N<sub>4</sub> SAC; adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on TM–N<sub>4</sub> SAC as a function of applied potential  $U$ , as well as PDOS of TM active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{\text{trans}}$ ; adsorption energy diagram and CO<sub>2</sub> angle variation of the CO<sub>2</sub> physisorption and chemisorption on Hg-(100) facet, as well as the CO<sub>2</sub> chemisorption configuration on Hg-(100) facet and CO<sub>2</sub> radical anion configuration in solvation environment; linear relationships between the  $U_{\text{trans}}$  of CO<sub>2</sub> and 21 features; illustration of the CO<sub>2</sub>RR process on Ni–N<sub>4</sub> SAC; illustration of CO<sub>2</sub>RR through CO<sub>2</sub> chemisorption and the new HER mechanism pathway; CI-NEB diagram of \*COOH formation and competing \*H adsorption; comparison of Faradaic efficiencies between computation and experiment; PDOS projected onto COOH s- and p-states on Ni–N<sub>4</sub> SAC at  $-1.0$ ,  $-1.5$ ,  $-2.0$ , and  $-2.5$  V; free energy diagram of TM–N<sub>4</sub> SACs at  $U_{\text{trans}}$ ; parity plot comparing the calculated  $U_{\text{trans}}$  value with the experimental onset potential for CO yield decline; energy evolution and C–Ni distance variation on TM–N<sub>4</sub> SACs at  $U_{\text{trans}}$  under 300 K; values of  $U$  parameters for DFT calculations; spin examination for CO<sub>2</sub> adsorption on Ni–N<sub>4</sub> SAC; OMC-constrained energies of Ni–N<sub>4</sub> SAC with CO<sub>2</sub> chemisorption and physisorption;  $U_{\text{trans}}$  value of 3d TM–N<sub>4</sub> SACs; surface energy of seven low-index Hg facets; 2D SISSO model for full-set data; 1D SISSO model from LOOCV; 2D SISSO model from LOOCV; held-out prediction for each TM–N<sub>4</sub> system from LOOCV examinations (PDF)

Optimized structures (POSCAR) and trajectory files (XDATCAR) from fixed-electron-number AIMD simulations initialized from the corresponding CP-DFT states at  $U_{\text{trans}}$  (ZIP)

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◆L.L. and W.C. contributed equally to this work.

## Notes

The authors declare no competing financial interest.

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# **Decoding CO<sub>2</sub> Adsorption Modes and CO Yield Variation on TM-N<sub>4</sub> Single-Atom Catalysts *via* Constant-Potential Computation and Machine-Learning Investigation**

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## Part 1. Stable Hg surface and potential-dependent CO<sub>2</sub> adsorption

To place our analysis in experimental context, classical studies combining polarography and pulse radiolysis relevant to CO<sub>2</sub> activation are first summarized. Because the one-electron reduction of CO<sub>2</sub> to CO<sub>2</sub><sup>•-</sup> is irreversible and involves substantial structural reorganization from a linear to a bent geometry,<sup>1-4</sup> its thermodynamic reduction potential cannot be determined exactly from polarographic wave positions.<sup>2</sup> Classical polarographic studies reported an irreversible reduction wave for CO<sub>2</sub> at -2.22 V vs. SCE,<sup>5</sup> which serves as an experimental reference rather than a true thermodynamic value. Complementary pulse-radiolysis experiments generated CO<sub>2</sub><sup>•-</sup> independently and, when combined with polarographic detection, revealed an oxidation wave for CO<sub>2</sub><sup>•-</sup> at -1.34 V vs. SCE.<sup>6</sup> On this basis, Koppenol and Rush estimated that the reduction potential of the CO<sub>2</sub>/CO<sub>2</sub><sup>•-</sup> couple lies between -2.22 and -1.34 V vs. SCE, corresponding to -1.98 and -1.10 vs. NHE (≈SHE).<sup>2</sup> These measurements provide an experimental reference for assessing theoretical descriptions of CO<sub>2</sub> activation on mercury (Hg) surface under a strongly reducing potential.

Since CO<sub>2</sub> reduction in polarographic measurements is generally understood to occur on the freshly renewed surface of the dropping Hg electrode, we next modeled CO<sub>2</sub> adsorption on polarized Hg surfaces to evaluate the corresponding reduction potential. Although Hg is liquid at room temperature, herein we employed a crystalline Hg structure from the Materials Project database<sup>7,8</sup> (MP-123, space group R-3m) as a simplified model for the local short-range order in liquid Hg.

We first determined the most stable Hg surface by evaluating the surface energies of seven low-index facets, including (100), (010), (001), (110), (101), (011), and (111). The surface energy ( $E_{sur}$ ) was evaluated as the sum of the cleavage energy ( $E_{cleave}$ ) and relaxation energy ( $E_{relax}$ ). The cleavage energy corresponds to the energy required to cleave a surface slab from the bulk structure, while the relaxation energy represents the energy decrease obtained after structural relaxation of the cleaved slab. The  $E_{sur}$ ,  $E_{cleave}$ , and  $E_{relax}$  were therefore calculated as:

$$E_{sur} = E_{cleave} + E_{relax} \quad (s1)$$

$$E_{cleave} = (E_{scf} - n \times E_{bulk}) / (2S) \quad (s2)$$

$$E_{relax} = (E_{opt} - E_{scf}) / S \quad (s3)$$

where  $S$  is the surface area,  $n$  is the number of atoms in the slab, the factor of 2 accounts for the two exposed surfaces, while  $E_{bulk}$ ,  $E_{scf}$ , and  $E_{opt}$  denote the energies of bulk Hg per atom, and of the cleaved slab before and after geometry optimizations, respectively.

The calculated surface energies for the seven Hg facets are summarized in **Table S9**. Among the examined surfaces, the Hg-(100) facet exhibits the lowest surface energy, indicating that it is the most stable termination. Accordingly, the Hg-(100) surface was selected for subsequent CO<sub>2</sub> adsorption energy calculations. To simulate the CO<sub>2</sub> activation potential observed in polarographic measurements on the dropping Hg electrode, constant-potential calculations were carried out to evaluate the Landau free energies of CO<sub>2</sub> physisorption and chemisorption on the Hg-(100) surface at various applied potentials.

The calculated results shown in **Figure S22a** indicate that the physisorption energy of CO<sub>2</sub> remains nearly constant across the investigated potential range, whereas the chemisorption energy progressively stabilizes as the electrode potential becomes more negative. This stabilization is accompanied by progressive CO<sub>2</sub> bending (**Figure S22b**), with the molecule adopting a bent geometry in the chemisorbed state (**Figure S22c**), resembling the geometry of the free CO<sub>2</sub><sup>•-</sup> radical stabilized by solvation (**Figure S22d**). Specifically, the transition from an unfavorable to a favorable chemisorption state occurs at a crossover potential defined as  $U_{trans} = -1.89$  V (vs. SHE), which falls within the experimentally inferred range of -1.98 to -1.10 V for the CO<sub>2</sub>/CO<sub>2</sub><sup>•-</sup> couple.

This agreement supports the interpretation that dropping Hg electrode acts as the catalytic surface for CO<sub>2</sub> activation in polarographic measurements and further establishes  $U_{trans}$  as a physically meaningful descriptor.

## Part 2. Derivation of electron hopping rate using the Fermi Golden Rule and the Newns-Anderson model

The use of Fermi's golden rule (FGR) combined with the Newns-Anderson (NA) model to estimate electron transfer (hopping) rates in electrocatalysis was first introduced by Nørskov and coworkers and later refined by Strasser, Chan, and coworkers.<sup>9,10</sup> However, those treatments did not provide a full derivation and primarily focused on adsorbates with projected density of states (PDOS) peaks at the Fermi level, and did not consider cases of off-Fermi DOS peaks and gapped (semiconducting) adsorbates. Here, we present a complete and transparent derivation to bridge this gap and generalize the formalism to both conducting and semi-conducting adsorbates.

### 2.1 Fermi Golden Rule

To quantify the electron hopping rate in electrocatalysis, we begin with the FGR, which provides the transition rate ( $k$ ) for an electron moving from an initial state  $|i\rangle$  to a final state  $|j\rangle$ . The general expression is:

$$k = \frac{2\pi}{\hbar} |\langle j|\hat{H}'|i\rangle|^2 \rho(\varepsilon_j) = \frac{2\pi}{\hbar} |V_{ij}|^2 \rho(\varepsilon_j) \quad (\text{s4})$$

where  $\hat{H}'$  is the perturbation Hamiltonian responsible for the transition,  $V_{ij}$  is the coupling matrix element between the two states, and  $\rho(\varepsilon_j)$  is the density of final states at the energy  $\varepsilon_j$ . Since FGR is derived from time-dependent perturbation theory, it is applicable in weak-coupling systems, typically associated with physisorption or weak chemisorption.

### 2.2 Combined with Newns-Anderson Model

To evaluate the coupling matrix element  $V_{ij}$ , we then employ the NA model, which describes the interaction between a localized adsorbate orbital and the continuum of metallic states on the catalyst. In this framework, the total Hamiltonian is decomposed into three components:

$$\hat{H} = \hat{H}_{ads} + \hat{H}_{cat} + \hat{H}_{coupling} \quad (\text{s5})$$

with



$$\hat{H}_{ads} = \varepsilon_a |a\rangle\langle a| \quad (s6)$$

$$\hat{H}_{cat} = \sum_k \varepsilon_k |k\rangle\langle k| \quad (s7)$$

$$\hat{H}_{coupling} = \sum_k (V_k |k\rangle\langle a| + V_k^* |a\rangle\langle k|) \quad (s8)$$

where  $\hat{H}_{ads}$  represents the isolated adsorbate,  $\hat{H}_{cat}$  accounts for the electronic structure of the catalyst, and the  $\hat{H}_{coupling}$  captures the interaction between adsorbate and catalyst.  $|a\rangle$  and  $|k\rangle$  are the adsorbate state and orthonormal basis for the catalyst states, respectively;  $\varepsilon_a$  and  $\varepsilon_k$  are the energy level of adsorbate and each metal states on catalyst;  $V_k$  and  $V_k^*$  are the coupling matrix between adsorbate and catalyst. Physically, the Hamiltonian must be Hermitian and satisfy the  $\hat{H} = \hat{H}^\dagger$ , therefore,  $\hat{H}_{coupling}$  should be composed by two parts:  $V_k |k\rangle\langle a|$  and  $V_k^* |a\rangle\langle k|$ . In electrocatalysis, the  $\sum_k V_k |k\rangle\langle a|$  accounts for the case that taking an electron from the adsorbate  $|a\rangle$  and move it into the catalyst  $|k\rangle$ , while the  $\sum_k V_k^* |a\rangle\langle k|$  represents the electron transfer direction from catalyst to adsorbate. Their combination represents the electron donation and back-donation in chemistry. In contrast to the FGR, Eq. (s5) treats coupling non-perturbatively, allowing it to capture the full range of chemisorption, from weak to strong.

To investigate the adsorbate level change with catalyst interaction, we employed the Green's function operator:

$$G(\varepsilon) = (\varepsilon + i\eta - \hat{H})^{-1} \quad (s9)$$

where  $\varepsilon$  is the energy variable and  $\eta \rightarrow 0^+$  is a small positive infinitesimal introduced to ensure convergence. The projected Green's function onto the adsorbate is

$$G_a(\varepsilon) = \langle a | (\varepsilon + i\eta - \hat{H})^{-1} | a \rangle \quad (s10)$$

Define:

$$|G_a\rangle = G(\varepsilon)|a\rangle \quad (s11)$$

Since the Hilbert space of the system (adsorbate + catalyst) is spanned over the states  $|a\rangle$  and all catalyst states  $|k\rangle$ , we can expand the vector  $|G_a\rangle$  as:

$$|G_a\rangle = \alpha|a\rangle + \sum_k \beta_k|k\rangle \quad (\text{s12})$$

Combine the Eqs. (s9) and (s11), we can get:

$$(\varepsilon + i\eta - \hat{H})|G_a\rangle = |a\rangle \quad (\text{s13})$$

Combine the Eqs. (s5-s8) and (s11-s12), then:

$$(\varepsilon + i\eta - \varepsilon_a)\alpha - \sum_k V_k^* \beta_k = 1 \quad (\text{s14})$$

$$(\varepsilon + i\eta - \varepsilon_k)\beta_k - V_k \alpha = 0 \quad (\text{s15})$$

Therefore,

$$\beta_k = \frac{V_k \alpha}{\varepsilon + i\eta - \varepsilon_k} \quad (\text{s16})$$

Insert  $\beta_k$  into Eq. (s14):

$$(\varepsilon + i\eta - \varepsilon_a)\alpha - \sum_k \frac{|V_k|^2 \alpha}{\varepsilon + i\eta - \varepsilon_k} = 1 \quad (\text{s17})$$

$$\alpha = \frac{1}{\varepsilon + i\eta - \varepsilon_a - \sum(\varepsilon)} \quad (\text{s18})$$

where

$$\sum(\varepsilon) = \sum_k \frac{|V_k|^2}{\varepsilon + i\eta - \varepsilon_k} \quad (\text{s19})$$

Thus, the projected Green function is:

$$G_a(\varepsilon) = \langle a|G(\varepsilon)|a\rangle = \frac{1}{\varepsilon + i\eta - \varepsilon_a - \sum(\varepsilon)} \quad (\text{s20})$$

It described how the adsorbate state is modified due to the interaction with catalyst. Therefore, based on the quantum many-body theory, the PDOS on the adsorbate can be obtained from the imaginary part of the projected Green function as:

$$\rho_a(\varepsilon) = -\frac{1}{\pi} \text{Im}G_a(\varepsilon) = \frac{1}{\pi} \cdot \frac{\Delta(\varepsilon)}{(\varepsilon - \varepsilon_a - \Lambda(\varepsilon))^2 + \Delta(\varepsilon)^2} \quad (\text{s21})$$

where  $\Lambda(\varepsilon)$  and  $\Delta(\varepsilon)$  are the real and imaginary part of  $\sum(\varepsilon)$  (self-energy), presenting the energy shift and level broadening of adsorbates, respectively. The  $\Delta(\varepsilon)$  can be expressed as:

$$\Delta(\varepsilon) = -\text{Im} \left[ \sum_k (\varepsilon) \right] = \pi \sum_k |V_k|^2 \delta(\varepsilon - \varepsilon_k) \quad (\text{s22})$$

For the ideal adsorbate-catalyst systems with weak to moderate coupling,  $\Delta(\varepsilon)$  is mostly negligible, thus Eq. (s21) can be simplified as:

$$\rho_a(\varepsilon) \approx \frac{1}{\pi} \cdot \frac{\Delta(\varepsilon)}{(\varepsilon - \varepsilon_a)^2 + \Delta(\varepsilon)^2} \quad (\text{s23})$$

This result takes the Lorentzian form:

$$L(x) = \frac{1}{\pi} \cdot \frac{\gamma}{(x - x_0)^2 + (\gamma)^2} \quad (\text{s24})$$

where  $\gamma$  is the width at half maximum of Lorentzian.

Therefore, we can relate peak broadening to hopping rate, if the adsorbate level  $\varepsilon_a$  is aligned with the Fermi level  $\varepsilon_F$ . Then, the peak width at  $\varepsilon_F$  reflects the coupling strength, and the electron hopping rate expression becomes:

$$k = \frac{2}{\hbar} \Delta(\varepsilon_F) \quad (\text{s25})$$

where  $\Delta(\varepsilon_F)$  is the width at half maximum of the PDOS peak evaluated at  $\varepsilon_F$ .

In this derivation based on the NA model, two key assumptions are made to arrive at a simplified expression for the electron hopping rate. First, the coupling between the localized adsorbate orbital and the catalyst states is assumed to be weak to moderate, allowing the real part of the hybridization function ( $\Lambda(\varepsilon)$ ) to be neglected. Second, the analysis focuses on a single localized orbital near the  $\varepsilon_F$ , assuming it dominates the electron transfer process and neglecting contributions from other orbitals or thermal activated transitions.

Under these assumptions, the electron hopping rate simplifies to Eq. (s25). However, this simplified expression is only valid when the center of adsorbate DOS peak aligns with  $\varepsilon_F$ . When the peak is shifted away from the  $\varepsilon_F$  while still overlapping via its tail, the simplified formula significantly overestimates the actual hopping rate. In addition, this expression cannot be applied to systems with semiconducting adsorbates, where  $\varepsilon_F$  lies within a band gap and no available DOS exists to support direct hopping. These limitations motivate us to develop a more generalized framework to describe electron transfer in such off-resonant or gapped systems.

### 2.3 Energy-shift-corrected electron hopping rate

To address the limitation of the standard hopping rate expression, for systems where the adsorbate DOS is not centered at the Fermi level, we re-consider the effect of energy shift on the electron transfer process. In more general cases, the center of projected DOS on adsorbate may not be fully aligned with  $\varepsilon_F$ , but instead appears as a broadened peak centered at an energy  $\varepsilon_0$  with an energy shift  $\Lambda$  from the  $\varepsilon_F$ :

$$\varepsilon_F = \varepsilon_0 + \Lambda \quad (\text{s26})$$

For a Lorentzian-shaped DOS with maximum height  $\rho_0$  and half-width  $\Delta$ , the DOS form can be re-written as:

$$\rho(\varepsilon) = \frac{\rho_0 \cdot \Delta^2}{(\varepsilon - \varepsilon_0)^2 + \Delta^2} \quad (\text{s27})$$

the value of the DOS at the Fermi level is then given by:

$$\rho(\varepsilon_F) = \frac{\rho_0 \cdot \Delta^2}{\Lambda^2 + \Delta^2} \quad (\text{s28})$$

This result highlights that even when the tail of the adsorbate DOS overlaps with  $\varepsilon_F$ , the actual DOS at the  $\varepsilon_F$  is significantly reduced compared to the case with  $\Lambda = 0$ . Consequently, the electron hopping rate is suppressed in proportion to this reduced overlap. Substituting  $\rho(\varepsilon_F)$  into the FGR expression, we can renew it as:

$$k = \frac{2\pi}{\hbar} |V|^2 \rho(\varepsilon_F) = \frac{2\pi}{\hbar} |V|^2 \frac{\rho_0 \cdot \Delta^2}{\Lambda^2 + \Delta^2} \quad (\text{s29})$$

Alternatively,

$$\Delta(\varepsilon) = \pi |V|^2 \rho_0 \quad (\text{s30})$$

The final expression of electron hopping rate can be re-written as:

$$k = \frac{2}{\hbar} \Delta \cdot \frac{\Delta^2}{\Lambda^2 + \Delta^2} \quad (\text{s31})$$

This generalized expression reduces to the standard result Eq. (s25) when  $\Lambda = 0$ , and captures the suppression of hopping that occurs as the adsorbate state becomes energetically misaligned with  $\varepsilon_F$ .

Compared with the full derivation above, the electron hopping rate can also be expressed in a more compact but physically transparent form as:



$$k = \frac{2}{\hbar} \Delta \cdot \frac{\rho(\varepsilon_F)}{\rho_0} \quad (\text{s32})$$

where  $\rho(\varepsilon_F)$  is the adsorbate PDOS directly evaluated at the Fermi level and  $\rho_0$  is the maximum value of the adsorbate peak.

Combine with an ideal Lorentzian line shape:

$$\frac{\rho(\varepsilon_F)}{\rho_0} = \frac{\Delta^2}{\Lambda^2 + \Delta^2} \quad (\text{s33})$$

Eq. (s32) can reduce to Eq. (s31). More generally, Eq. (s32) remains valid for non-ideal Lorentzian line shapes, in which the ratio  $\frac{\rho(\varepsilon_F)}{\rho_0}$  can be directly obtained from DFT-calculated PDOS without assuming any specific functional form. Therefore, it provides a simpler and more model-independent correction in actual calculations.

## 2.4 Semiconducting electron hopping rate

The derivation above assumes a localized adsorbate orbital with finite DOS at the  $\varepsilon_F$ , allowing direct electron hopping. However, in systems where the adsorbate is semiconducting, the DOS vanishes at the  $\varepsilon_F$ , and direct hopping is suppressed. In such cases, electron transport must proceed through a thermally activated mechanism, which therefore requires an improved rate expression that includes thermal effects.

To account for the thermal effect, we extend the FGR integrating over the energy spectrum with incorporating the Fermi-Dirac distribution, defined as:

$$k = g \cdot \frac{2\pi}{\hbar} \int_{-\infty}^{+\infty} |V_\varepsilon|^2 \rho(\varepsilon) f(\varepsilon, T) d\varepsilon \quad (\text{s34})$$

where  $g = 2$  is the spin degeneracy factor, and  $f(\varepsilon, T)$  is the Fermi-Dirac distribution:

$$f(\varepsilon, T) = \frac{1}{e^{\varepsilon - \mu / k_B T} + 1} \quad (\text{s35})$$

Here,  $\mu$  is the chemical potential of electrons and  $T$  is the temperature. In the metallic limit, where  $\rho(\varepsilon_F)$  is non-zero, Eq. (s34) reduces to:

$$k \approx \frac{2\pi}{\hbar} |V|^2 \rho(\varepsilon_F) \quad (\text{s36})$$

recovering the expression of Eq. (s4). However, in the semiconducting case, the integral is

dominated by the tail of the valence band close to  $\varepsilon_F$ , requiring thermal excitation across the band gap  $\Delta E$ . Assuming the 1<sup>st</sup> peak below  $\varepsilon_F$  is centered at the valence band maximum (VBM), the electron hopping rate can be renewed as:

$$k \approx \frac{2}{\hbar} \Delta(\varepsilon_{VBM}) \cdot e^{-\frac{\Delta E}{k_B T}} \cdot k_B T \quad (\text{s37})$$

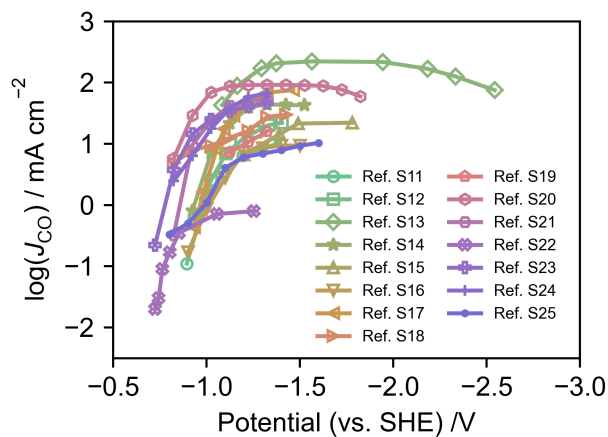
which follows Arrhenius-type behavior:

$$k \propto e^{-\frac{\Delta E}{k_B T}} \quad (\text{s38})$$

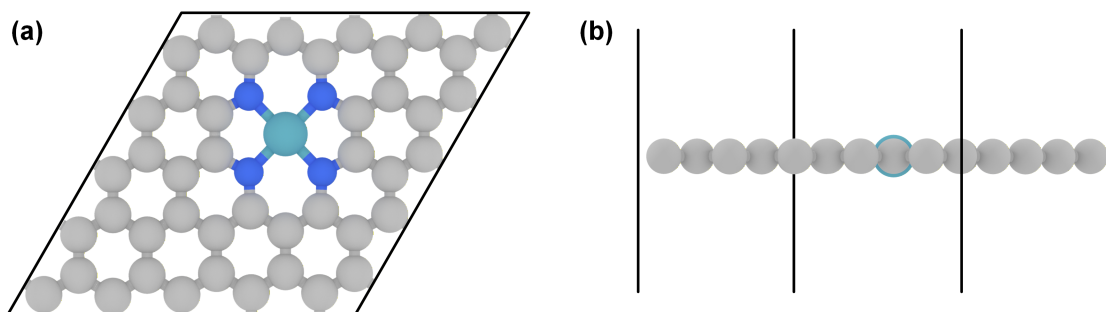
Therefore, the electron hopping rate can be summarized as:

$$k = \begin{cases} \frac{2}{\hbar} \Delta \cdot \frac{\rho(\varepsilon_F)}{\rho_0}, & \text{metallic} \\ \frac{2}{\hbar} \Delta(\varepsilon_{VBM}) \cdot e^{-\frac{\Delta E}{k_B T}} \cdot k_B T, & \text{semiconducting} \end{cases} \quad (\text{s39})$$

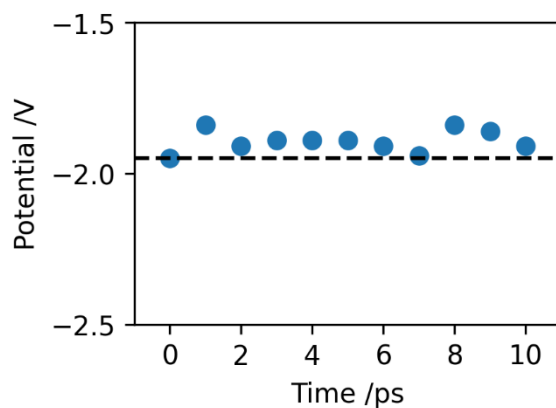
### Part 3. Figures and tables of the manuscript



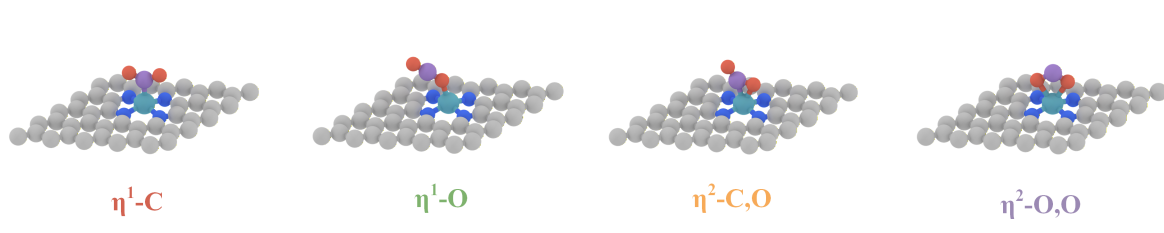
**Figure S1.** Experimental data set of CO partial current density as a function of applied potential (all converted to values versus SHE to enable comparison across different pH conditions).<sup>11-25</sup> Electrolyte and pH conditions in references are (1) 0.1 M KHCO<sub>3</sub> with pH 6.8: Ref. S15, S16, and S25; (2) 0.5 M KHCO<sub>3</sub> with pH 7.2: Ref. S11, S12, S14, S17-S21, S23, and S24; (3) 1 M KHCO<sub>3</sub> with pH 7.7: Ref. S13, and S22.



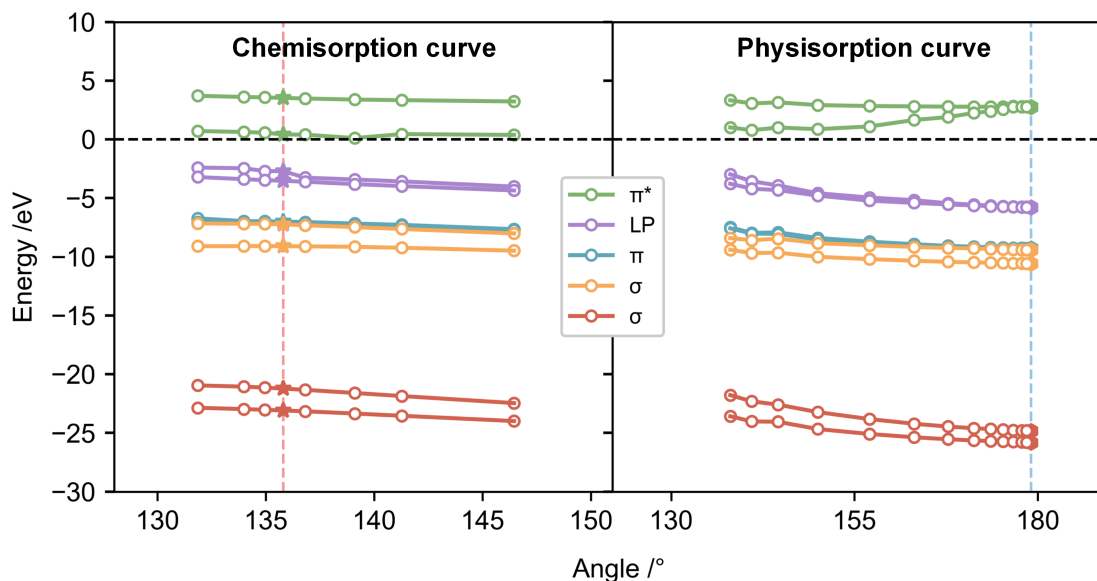
**Figure S2.** Structure model of TM-N<sub>4</sub> SACs. (a) Top view. (b) Side view. The C, N, and transition metal (TM) atoms are colored in gray, blue, and cyan, respectively.



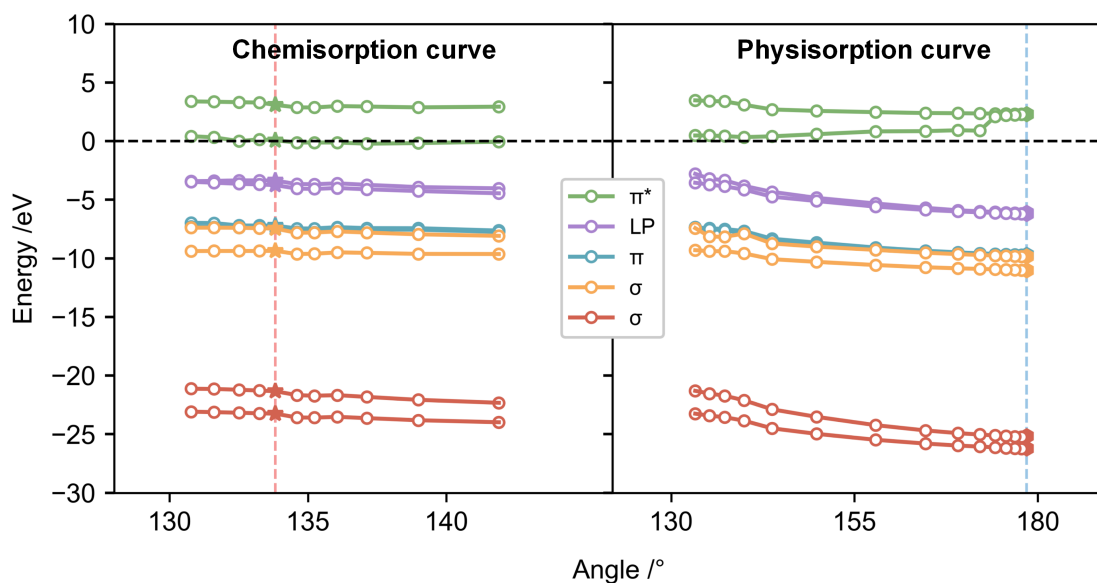
**Figure S3.** Validation of the fixed-number-electron AIMD treatment for chemisorbed CO<sub>2</sub> on Ni-N<sub>4</sub> at  $U_{\text{trans}} = -1.95$  V. Eleven snapshots, extracted at 1 ps intervals from a 10 ps AIMD trajectory, were used to evaluate the corresponding electrode potential. The inferred potential remains close to the target value, fluctuating only within -1.95 to -1.84 V, which supports the use of the CP-derived charge state for assessing the finite-temperature stability of the chemisorbed configuration.



**Figure S4.** Four possible CO<sub>2</sub> chemisorption configurations, including  $\eta^1\text{-C}$ ,  $\eta^1\text{-O}$ ,  $\eta^2\text{-C,O}$ , and  $\eta^2\text{-O,O}$ . The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, and TM atoms are shown in blue, red, and cyan, respectively.

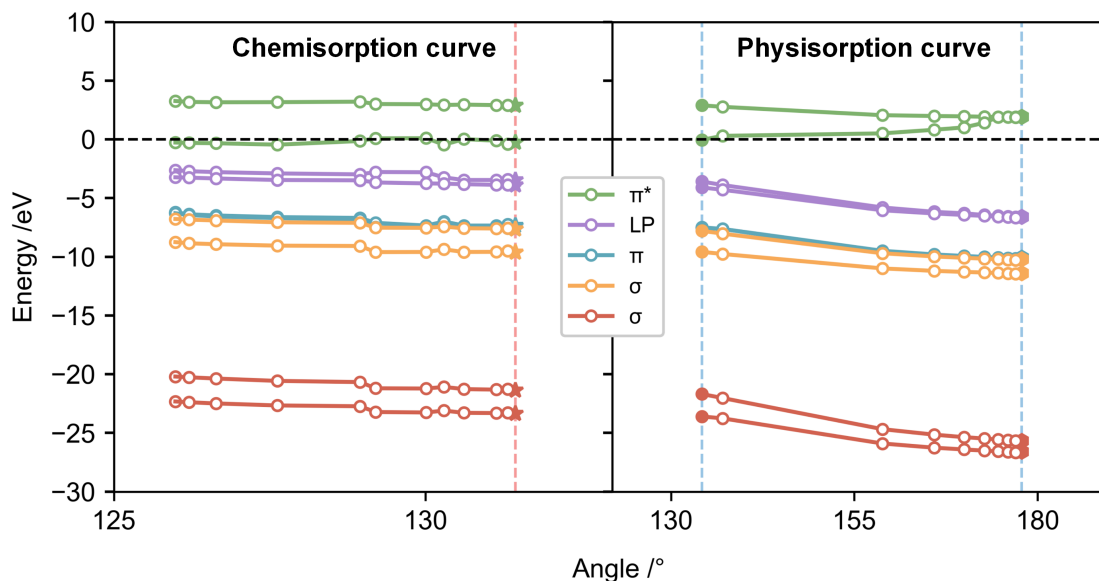


**Figure S5.** Walsh diagram for CO<sub>2</sub> at  $U = -1.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The curve for the  $\pi^*$  orbitals with relatively lower energy is the average value of multiple states straddling the Fermi level.

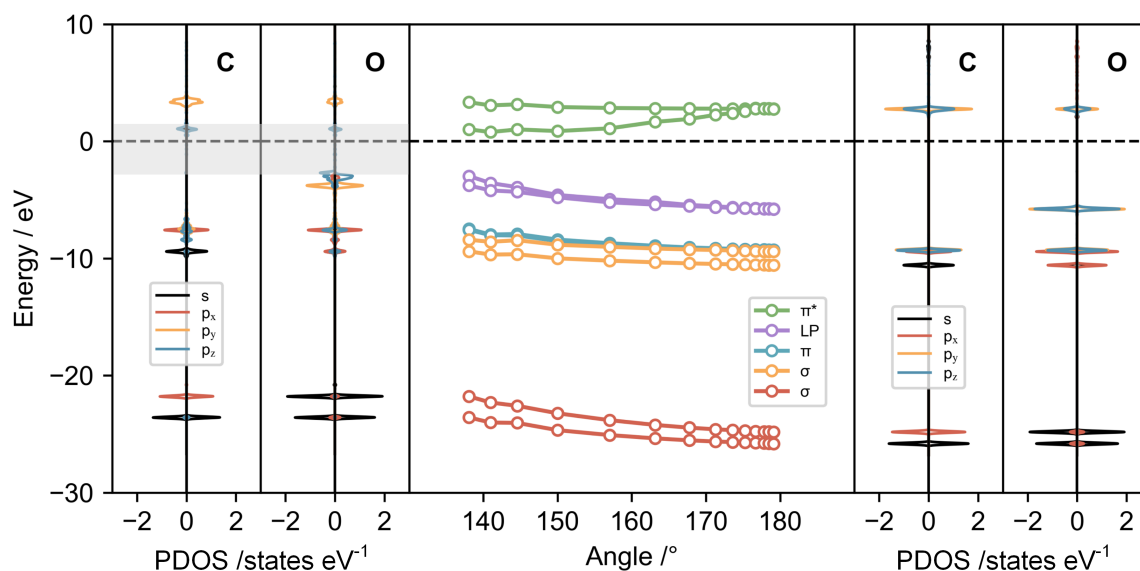


**Figure S6.** Walsh diagram for CO<sub>2</sub> at  $U = -2.0$  V vs. SHE on Ni-N<sub>4</sub> SAC. The curve for the  $\pi^*$  orbitals with relatively lower energy is the average value of multiple states straddling the Fermi level.

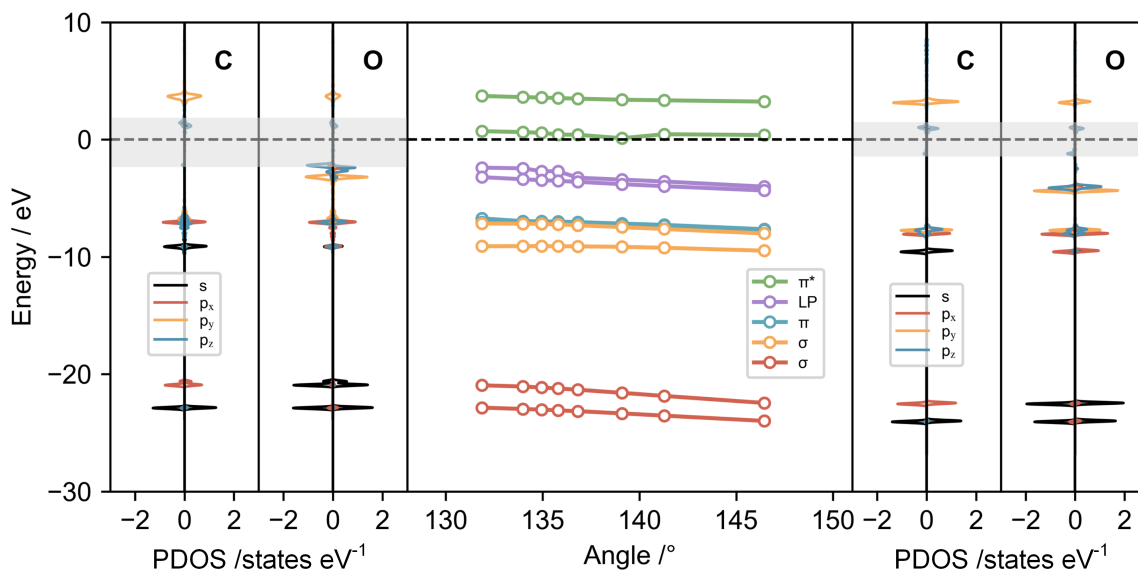




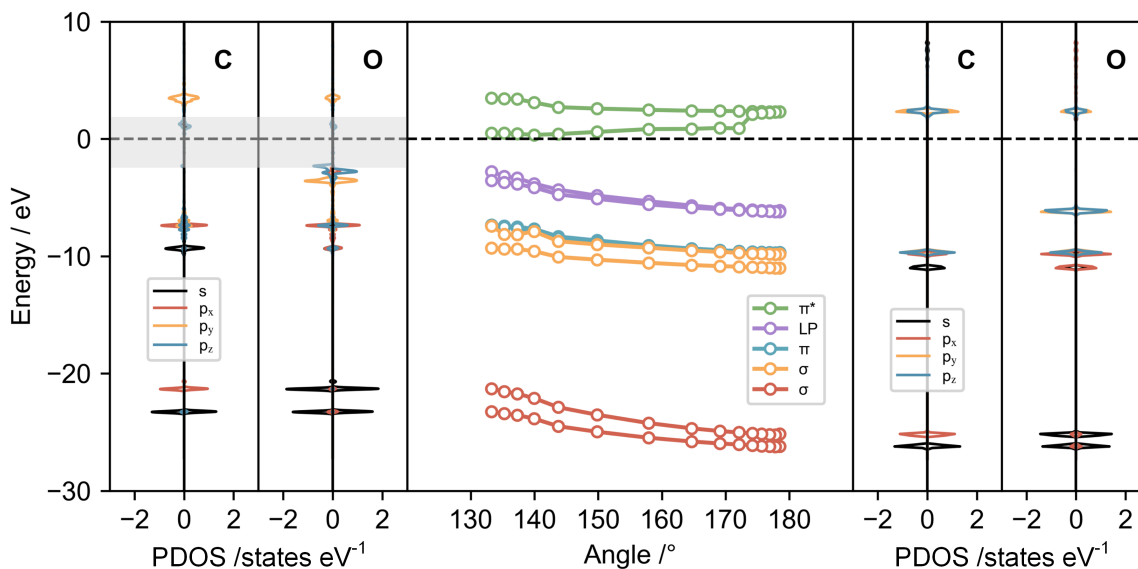
**Figure S7.** Walsh diagram for CO<sub>2</sub> at  $U = -2.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The curve for the  $\pi^*$  orbitals with relatively lower energy is the average value of multiple states straddling the Fermi level.



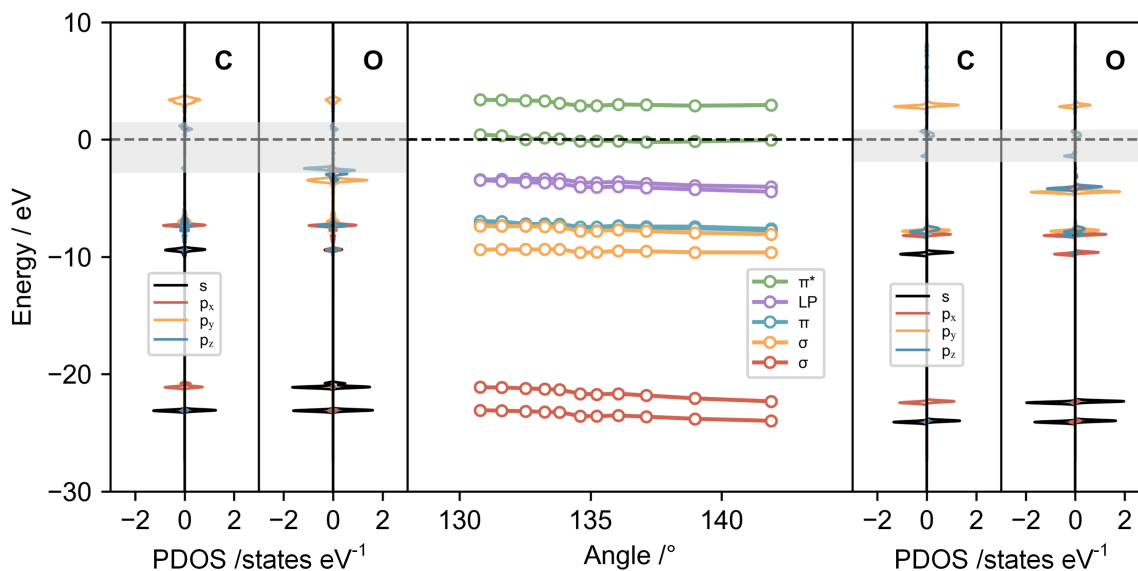
**Figure S8.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the physisorption curve at  $U = -1.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.



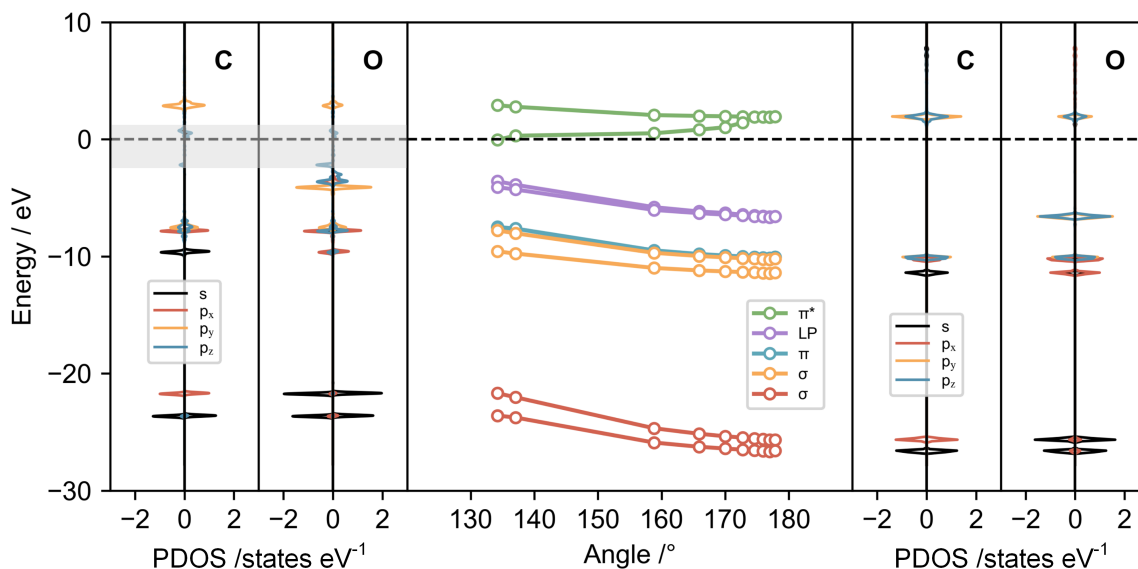
**Figure S9.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the chemisorption curve at  $U = -1.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.



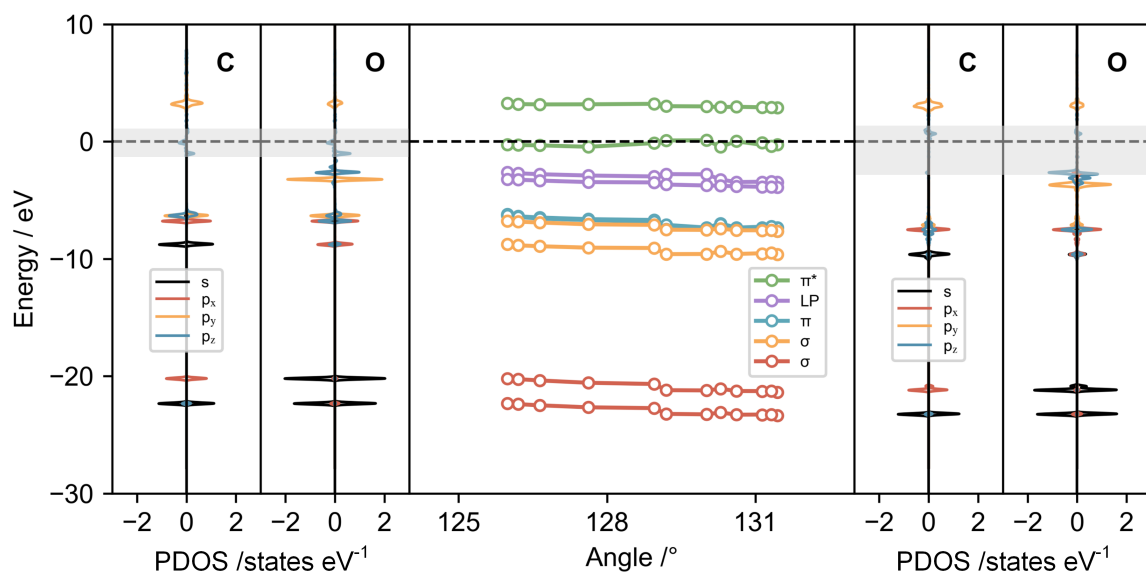
**Figure S10.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the physisorption curve at  $U = -2.0$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.



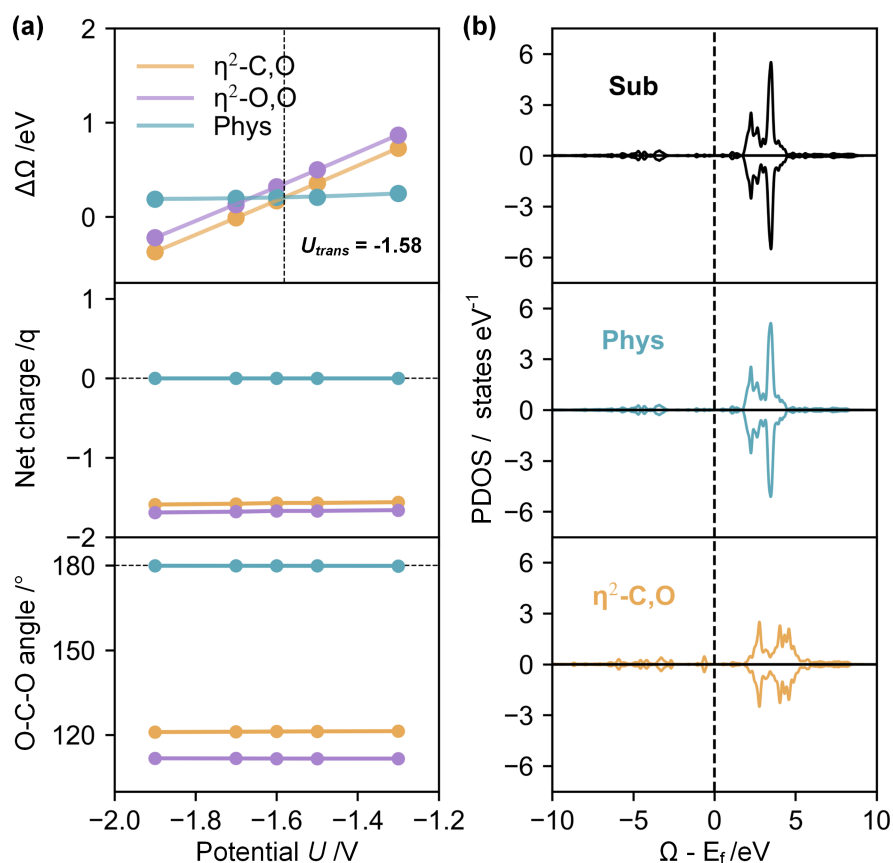
**Figure S11.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the chemisorption curve at  $U = -2.0$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.



**Figure S12.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the physisorption curve at  $U = -2.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.

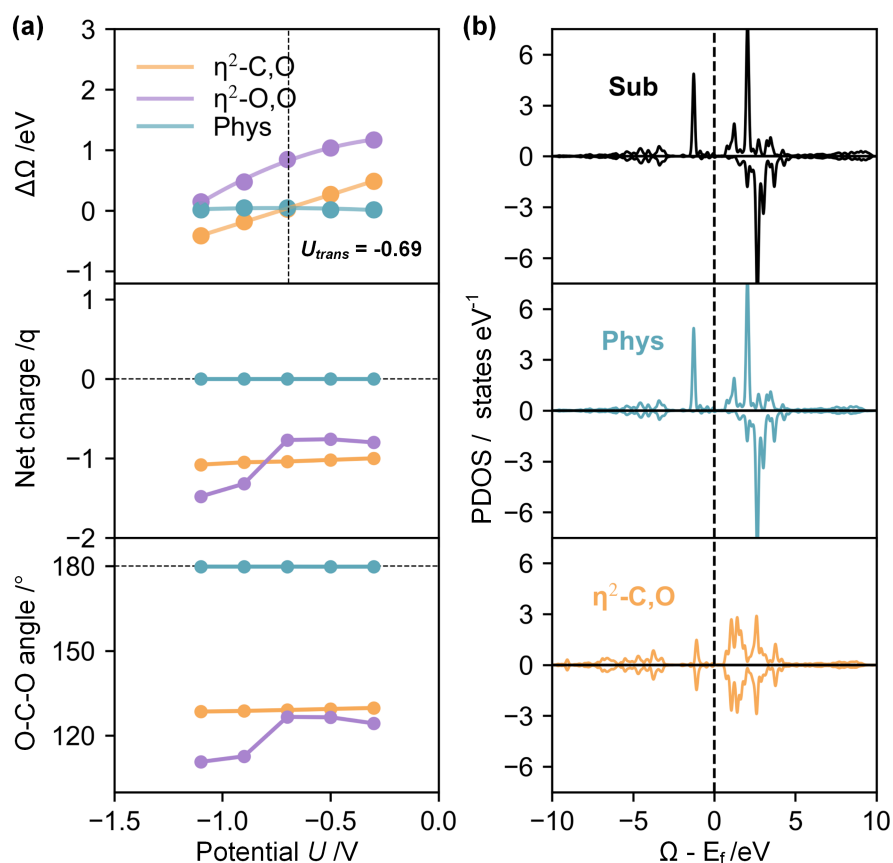


**Figure S13.** Walsh diagram with corresponding partial density (PDOS) of states of CO<sub>2</sub> along the chemisorption curve at  $U = -2.5$  V vs. SHE on Ni-N<sub>4</sub> SAC. The multiple lower-energy  $\pi^*$  states are located in the gray ribbon.

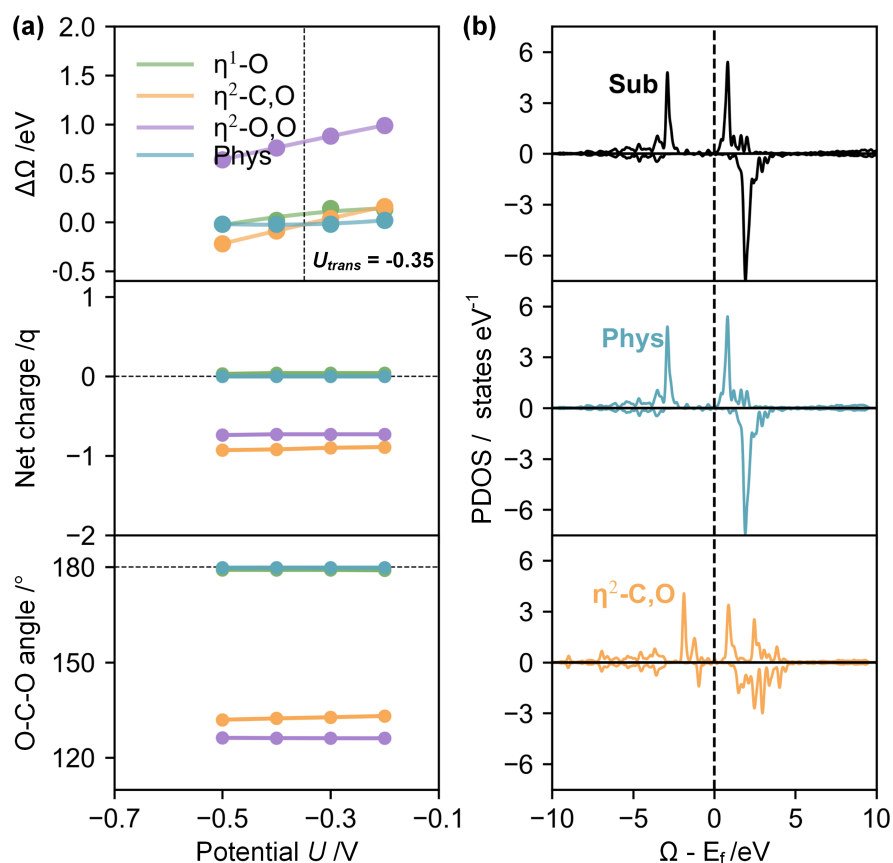


**Figure S14.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Sc-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Sc-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption can occur in  $\eta^2$ -C,O and  $\eta^2$ -O,O configurations, while the  $\eta^1$ -C and  $\eta^1$ -O modes transition to the  $\eta^2$ -C,O or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Sc active center before and after CO<sub>2</sub> physisorption/chemisorption at “transorption” potential ( $U_{trans}$ ).

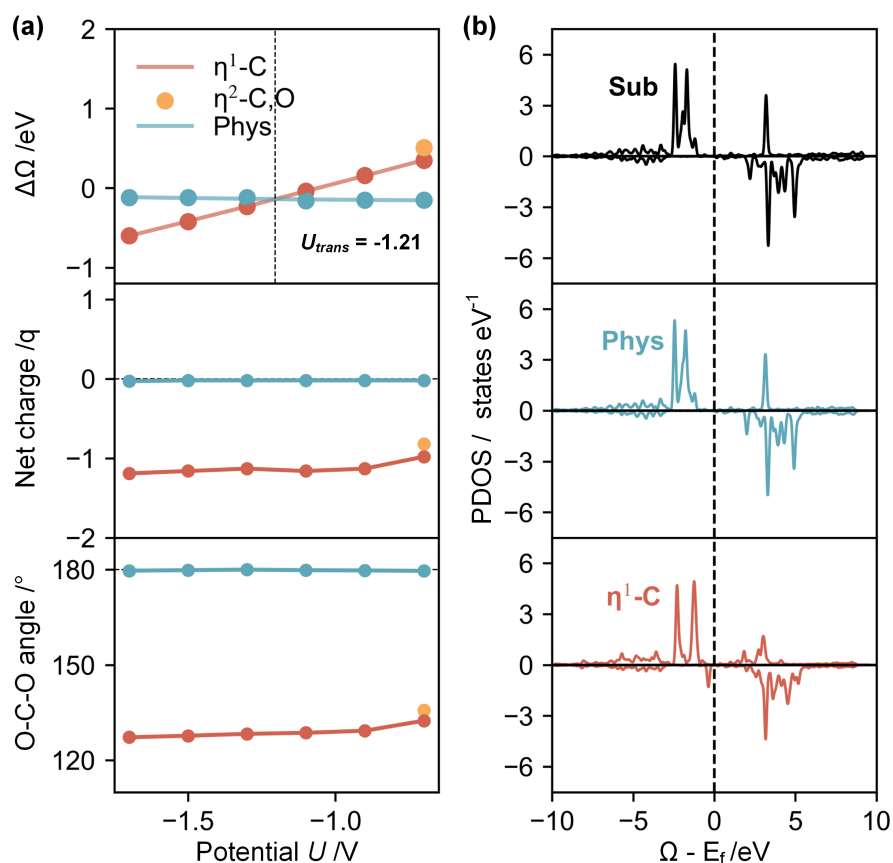




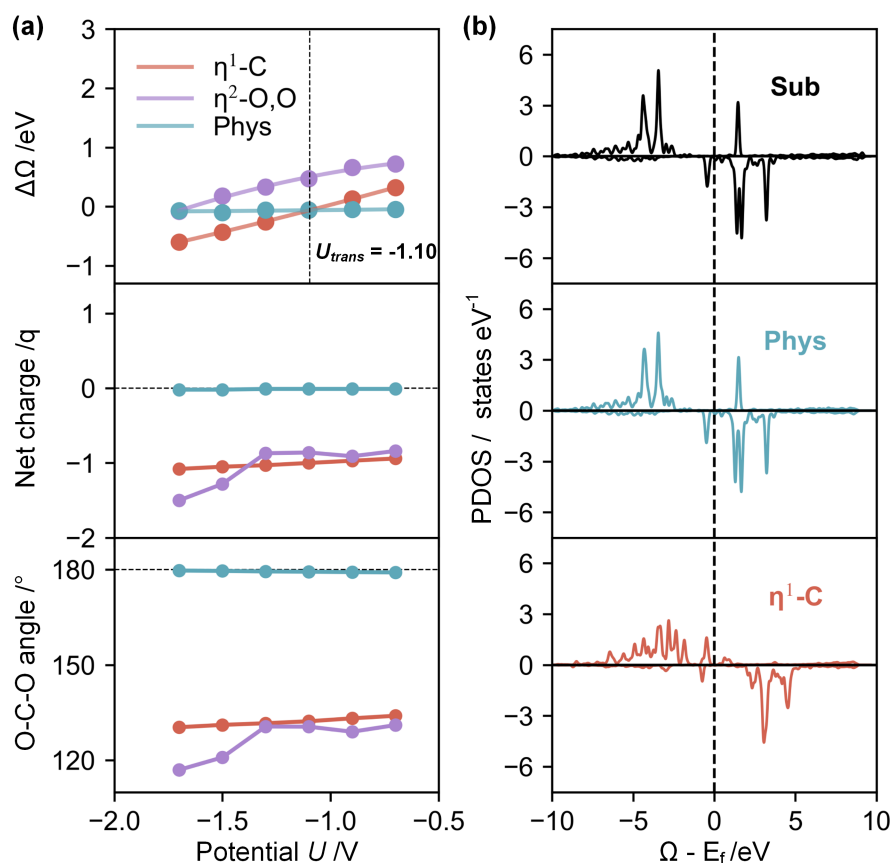
**Figure S15.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Ti-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Ti-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption can occur in  $\eta^2$ -C,O and  $\eta^2$ -O,O configurations, while the  $\eta^1$ -C and  $\eta^1$ -O modes transition to the  $\eta^2$ -C,O or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Ti active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .



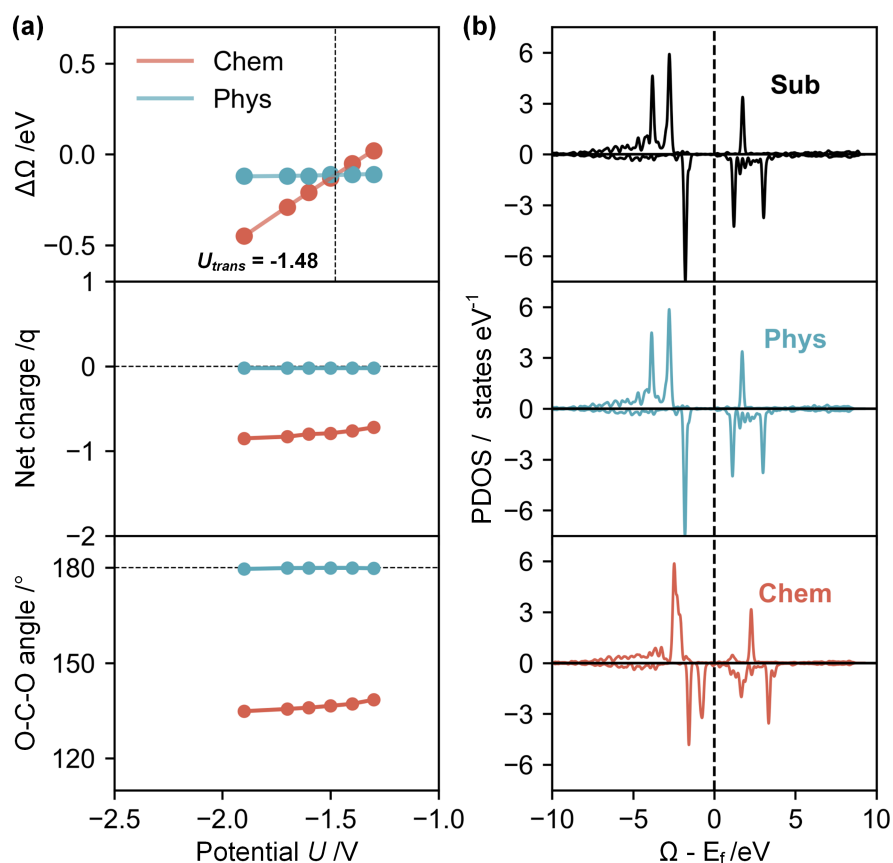
**Figure S16.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on V-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the V-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption can occur in  $\eta^1$ -O,  $\eta^2$ -C,O and  $\eta^2$ -O,O configurations, while the  $\eta^1$ -C mode transitions to the  $\eta^2$ -C,O or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the V active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .



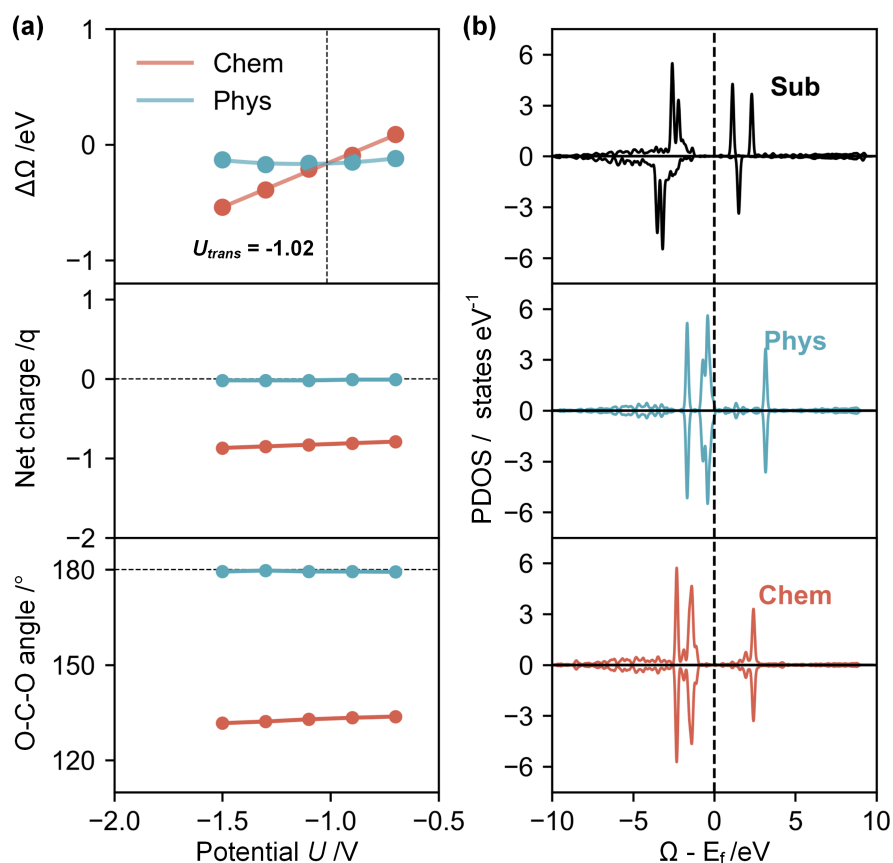
**Figure S17.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Cr-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Cr-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption mainly occurs in  $\eta^1$ -C configuration with our examined potential range and the  $\eta^2$ -C,O configuration is the only one other chemisorption mode observed at -0.7 V, while the different initial modes transition to the  $\eta^1$ -C or physisorption at various applied potentials after geometry optimization. (b) Partial density of states (PDOS) of the Cr active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .



**Figure S18.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Mn-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Mn-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption can occur in  $\eta^1$ -C and  $\eta^2$ -O,O configurations, while the  $\eta^1$ -O and  $\eta^2$ -C,O modes transition to the  $\eta^1$ -C or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Mn active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .

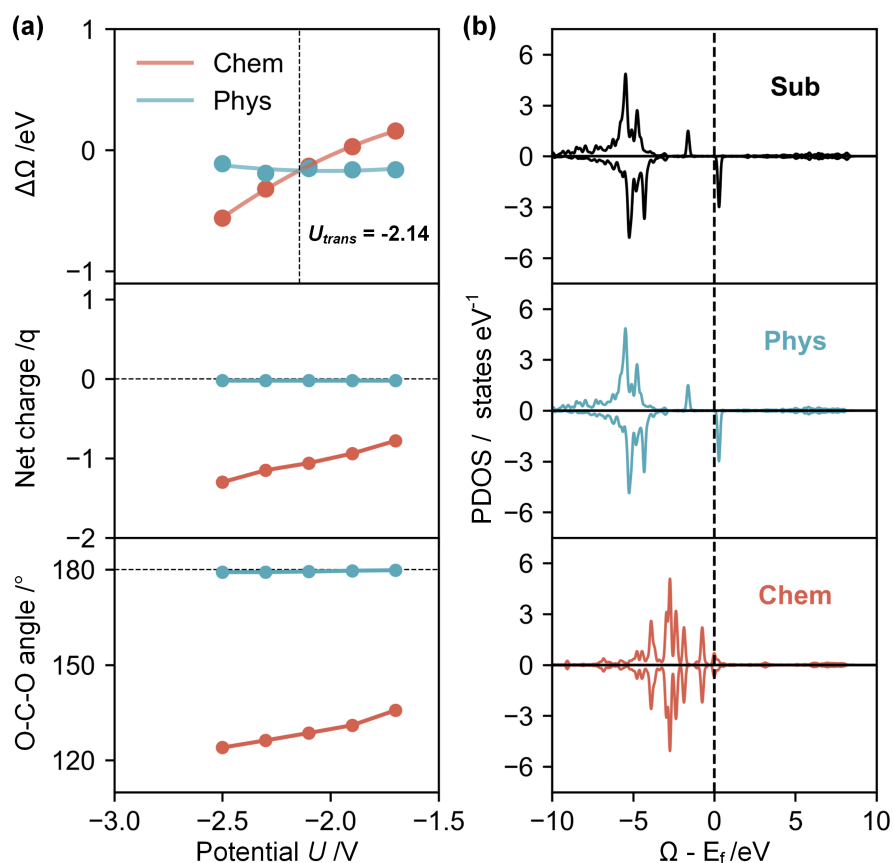


**Figure S19.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Fe-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Fe-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption only presents the stable  $\eta^1$ -C configuration, while the other three modes transition to the  $\eta^1$ -C or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Fe active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .

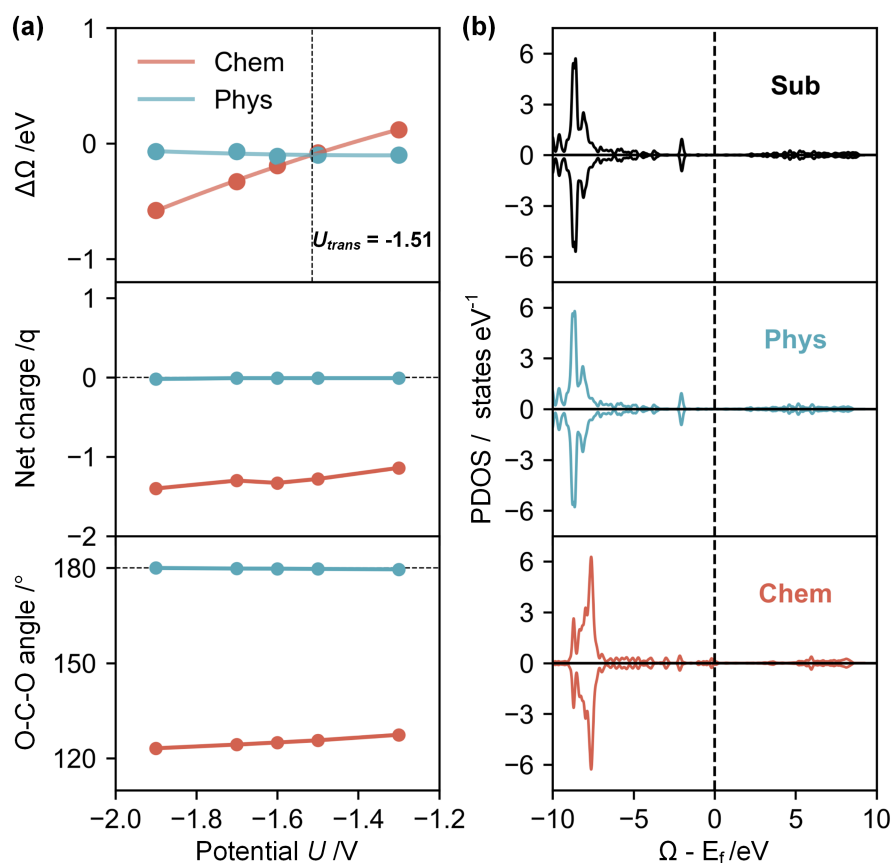


**Figure S20.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Co-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Co-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption only presents the stable  $\eta^1$ -C configuration, while the other three modes transition to the  $\eta^1$ -C or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Co active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .

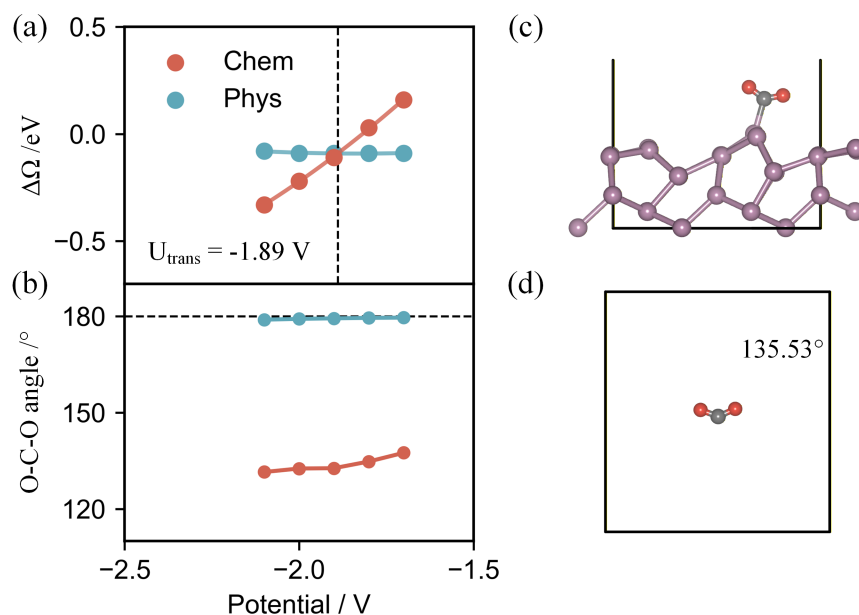




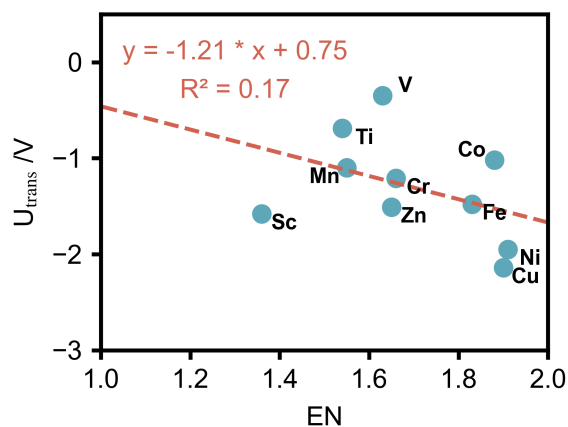
**Figure S21.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Cu-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Cu-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption only presents the stable  $\eta^1$ -C configuration, while the other three modes transition to the  $\eta^1$ -C or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Cu active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .



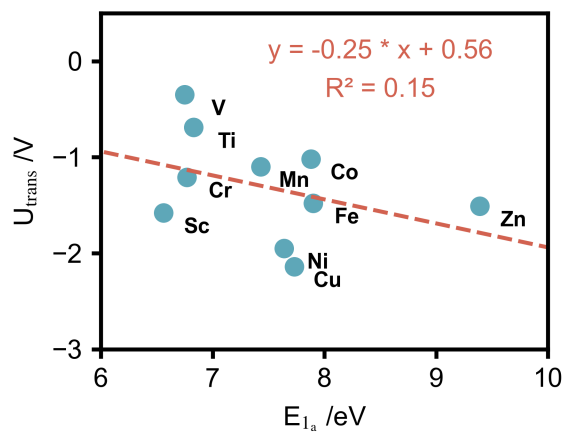
**Figure S22.** (a) Adsorption energy diagram, net charge transfer, and CO<sub>2</sub> angle variation for the minimum position on the physisorption and chemisorption curves on Zn-N<sub>4</sub> SAC as a function of applied potential  $U$ . For the Zn-N<sub>4</sub> SAC, CO<sub>2</sub> chemisorption only presents the  $\eta^1$ -C configuration, while the other three modes transition to the  $\eta^1$ -C or physisorption after geometry optimization. (b) Partial density of states (PDOS) of the Zn active center before and after the CO<sub>2</sub> physisorption/chemisorption at  $U_{trans}$ .



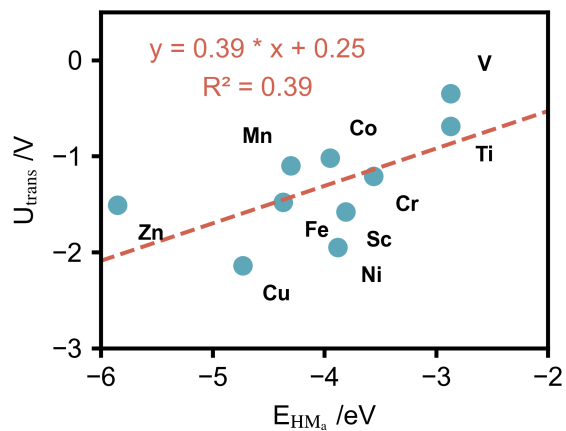
**Figure S23.** (a) Potential-dependent Landau adsorption free energies ( $\Delta\Omega$ ) of the CO<sub>2</sub> physisorption (blue) and chemisorption (red) on Hg-(100) facet. (b) O–C–O bond angle for the minimum-energy states along the physisorption and chemisorption curves. (c) Optimized structure of CO<sub>2</sub> chemisorbed on Hg-(100) facet, shown as a representative configuration at -1.9 V. (d) Optimized structure of CO<sub>2</sub> with one additional electron injected in the solvation environment. The C, O, and Hg atoms are shown in grey, red, and purple, respectively.



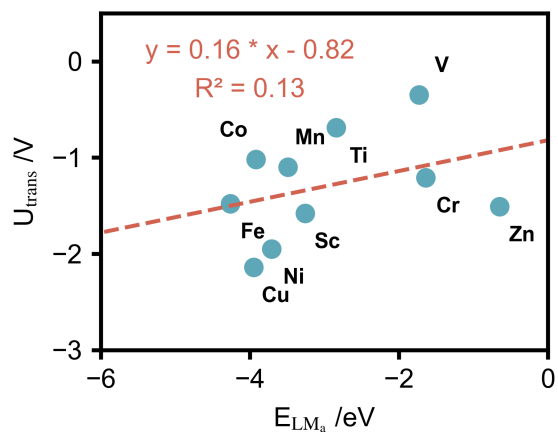
**Figure S24.** Linear relationship between  $U_{trans}$  and electronegativity.



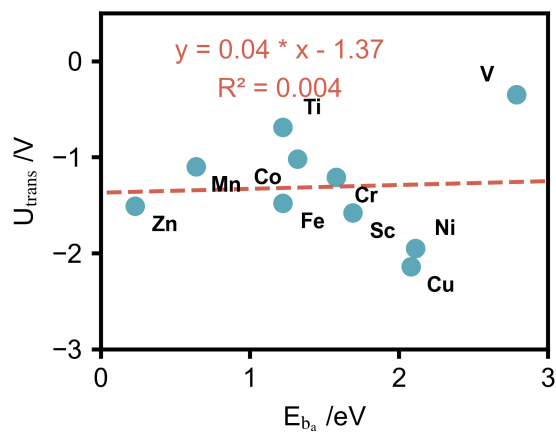
**Figure S25.** Linear relationship between  $U_{trans}$  and the first ionization energy.



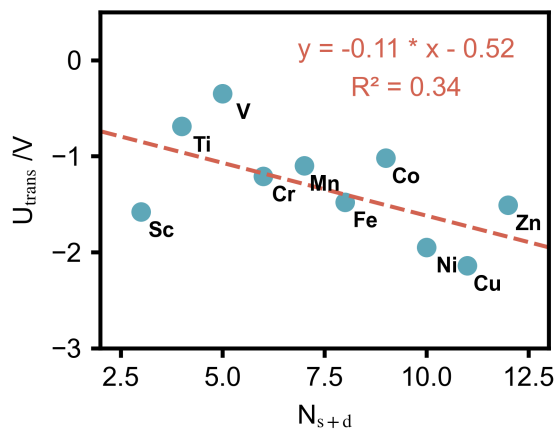
**Figure S26.** Linear relationship between  $U_{trans}$  and the highest occupied molecular orbital.



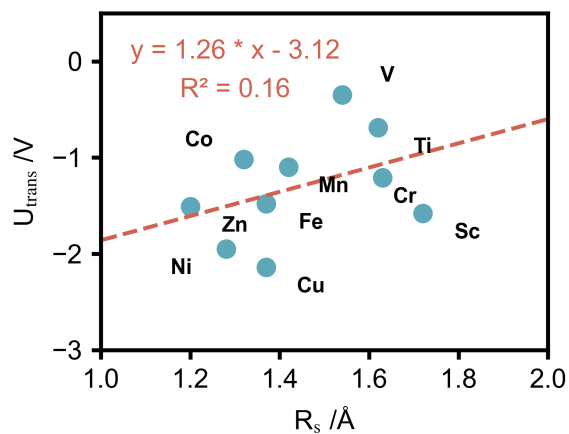
**Figure S27.** Linear relationship between  $U_{trans}$  and the lowest unoccupied molecular orbital.



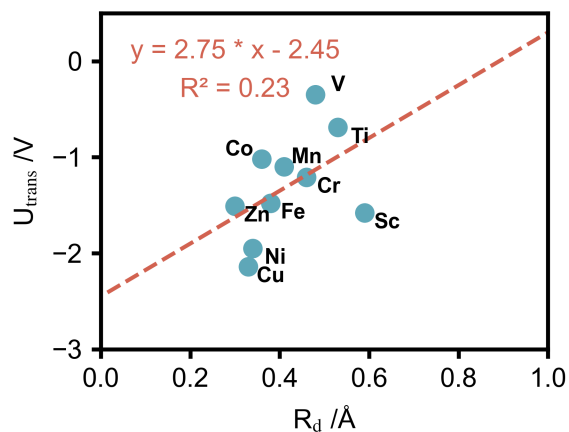
**Figure S28.** Linear relationship between  $U_{trans}$  and binding energy of metal dimer.



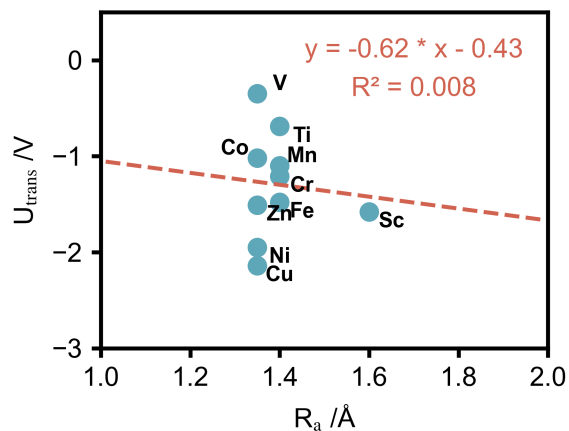
**Figure S29.** Linear relationship between  $U_{trans}$  and the electron numbers in d and s orbitals.



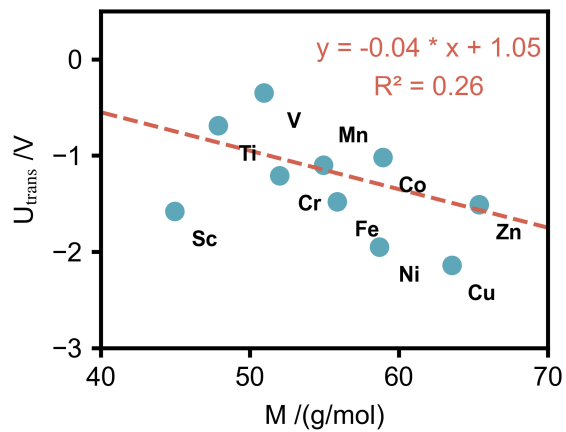
**Figure S30.** Linear relationship between  $U_{trans}$  and s orbital radius.



**Figure S31.** Linear relationship between  $U_{trans}$  and d orbital radius.

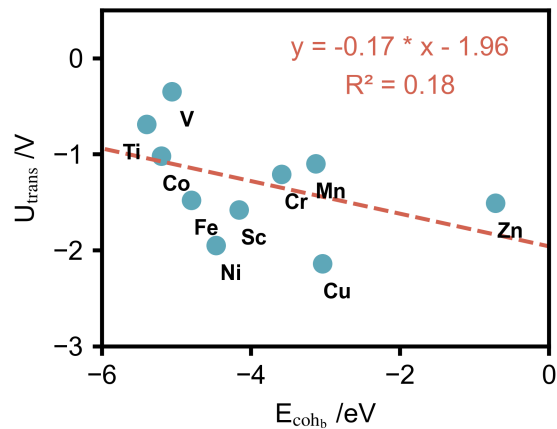


**Figure S32.** Linear relationship between  $U_{trans}$  and atomic radius.

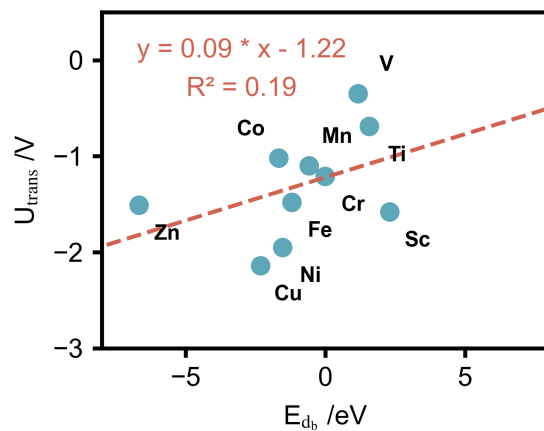


**Figure S33.** Linear relationship between  $U_{trans}$  and mass.

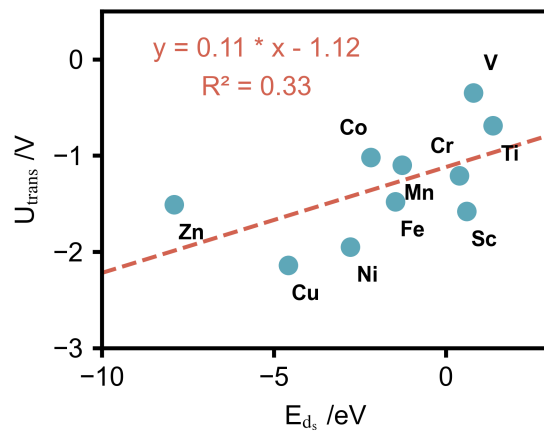




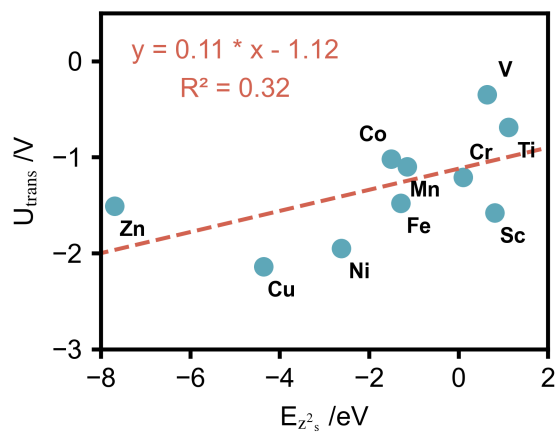
**Figure S34.** Linear relationship between  $U_{trans}$  and cohesive energy.



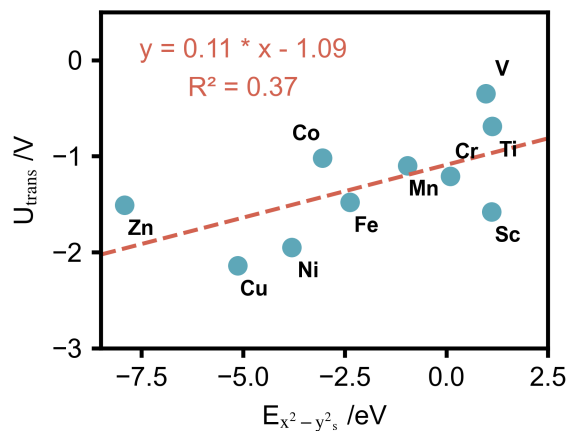
**Figure S35.** Linear relationship between  $U_{trans}$  and the energy of d-band center.



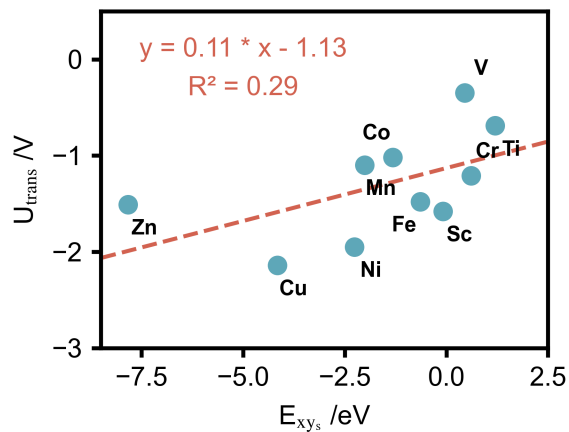
**Figure S36.** Linear relationship between  $U_{trans}$  and the energy of d-band center on SACs.



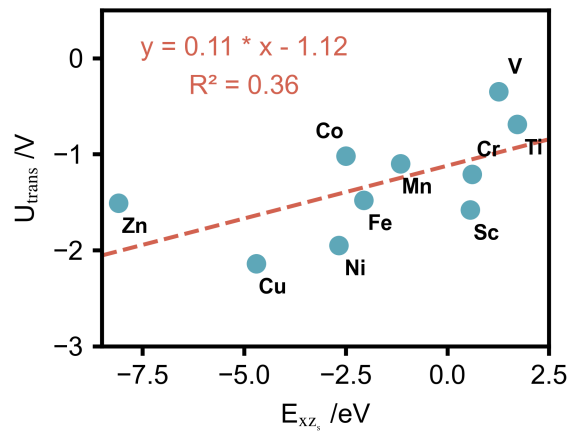
**Figure S37.** Linear relationship between  $U_{trans}$  and the energy of  $d_{z^2}$ -band center on SACs.



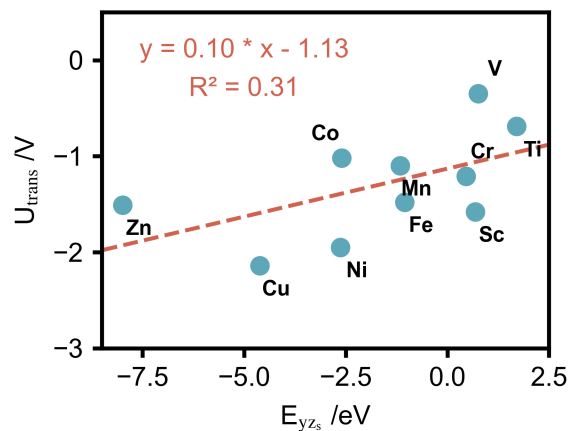
**Figure S38.** Linear relationship between  $U_{trans}$  and the energy of  $d_{x^2-y^2}$ -band center on SACs.



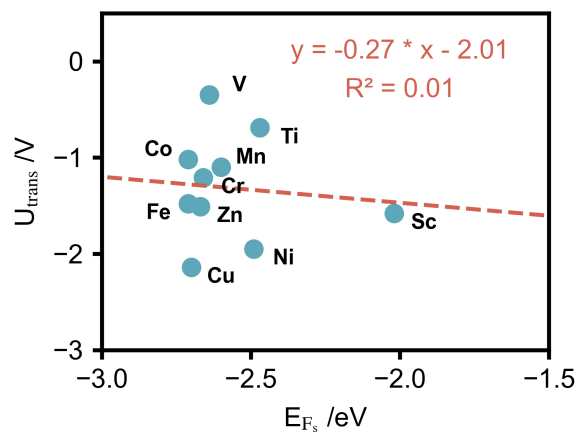
**Figure S39.** Linear relationship between  $U_{trans}$  and the energy of  $d_{xy}$ -band center on SACs.



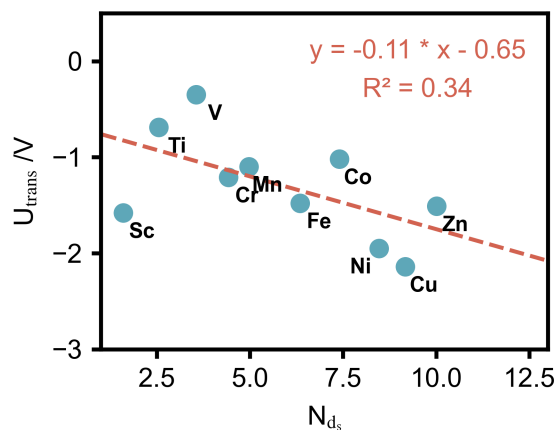
**Figure S40.** Linear relationship between  $U_{trans}$  and the energy of  $d_{xz}$ -band center on SACs.



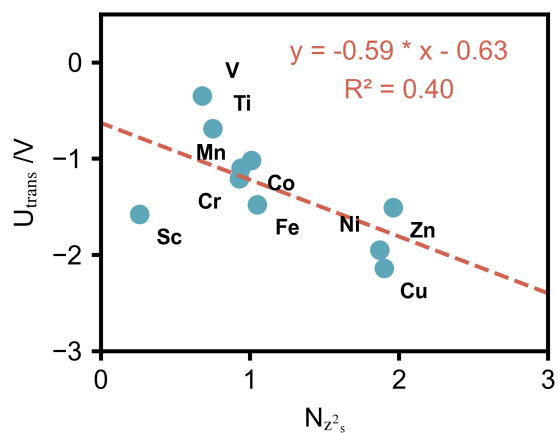
**Figure S41.** Linear relationship between  $U_{trans}$  and the energy of  $d_{yz}$ -band center on SACs.



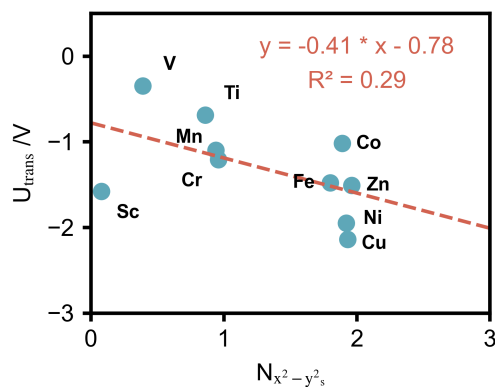
**Figure S42.** Linear relationship between  $U_{trans}$  and the Fermi energy on SACs.



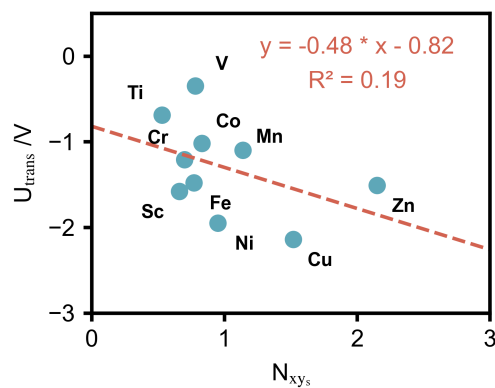
**Figure S43.** Linear relationship between  $U_{trans}$  and the electron number in d orbitals in grand state on SACs.



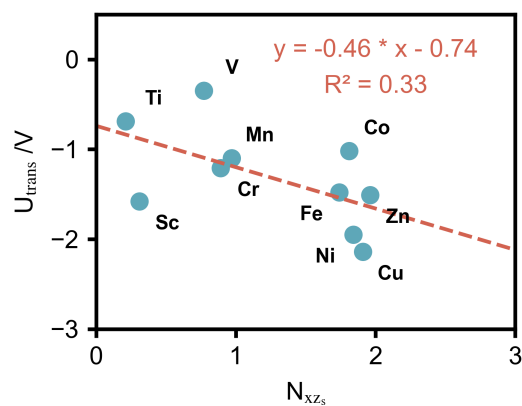
**Figure S44.** Linear relationship between  $U_{trans}$  and the electron number in  $d_{z^2}$  orbitals in grand state on SACs.



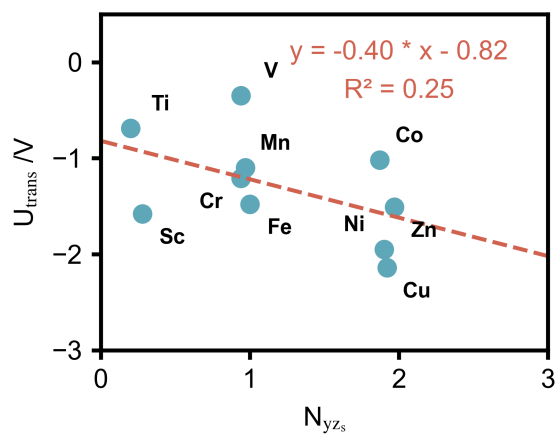
**Figure S45.** Linear relationship between  $U_{trans}$  and the electron number in  $d_{x^2-y^2}$  orbitals in the grand state on SACs.



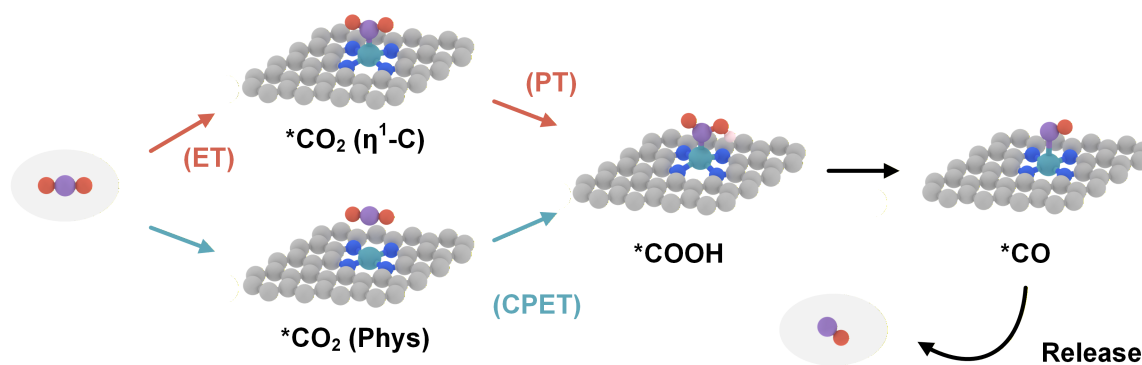
**Figure S46.** Linear relationship between  $U_{trans}$  and the electron number in  $d_{xy}$  orbitals in the grand state on SACs.



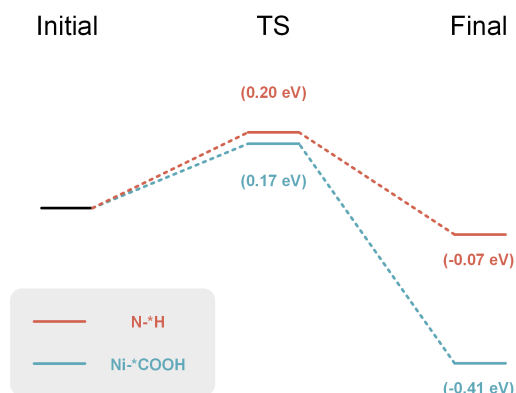
**Figure S47.** Linear relationship between  $U_{trans}$  and the electron number in  $d_{xz}$  orbitals in the grand state on SACs.



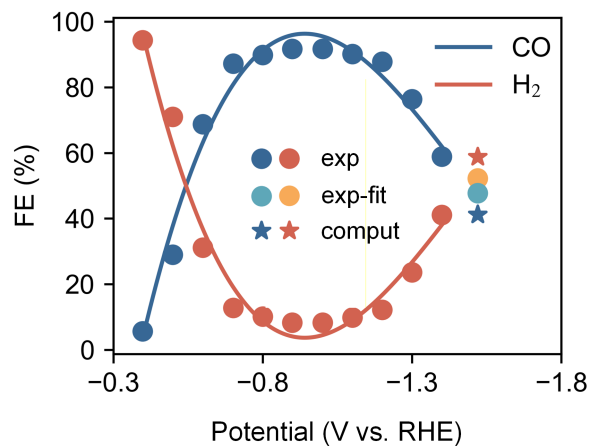
**Figure S48.** Linear relationship between  $U_{trans}$  and the electron number in  $d_{yz}$  orbitals in the grand state on SACs.



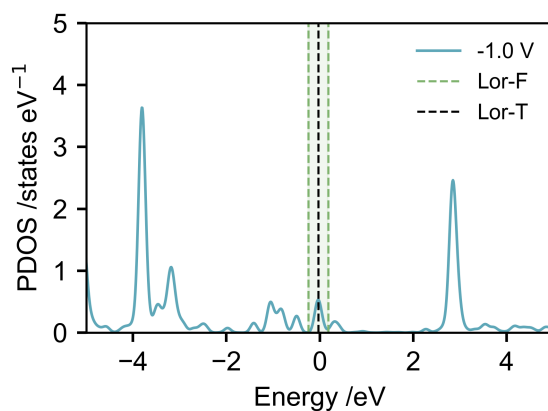
**Figure S49.** Illustration of CO<sub>2</sub>RR on Ni-N<sub>4</sub> SACs. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and TM atoms are shown in blue, red, pink, and cyan, respectively.



**Figure S50.** Reaction pathways for \*COOH formation and competing \*H adsorption on one of the four coordinating N sites of Ni-N<sub>4</sub> SAC. The computations were performed using the CI-NEB method within a commonly used hybrid solvation model,<sup>26,27</sup> in which 13 explicit H<sub>2</sub>O molecules were included to represent the local solvent environment and facilitate proton transfer.

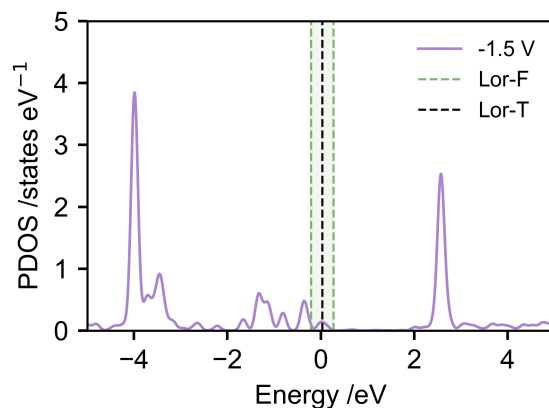


**Figure S51.** Comparison of Faradaic efficiencies between computation and experiment.<sup>20</sup>

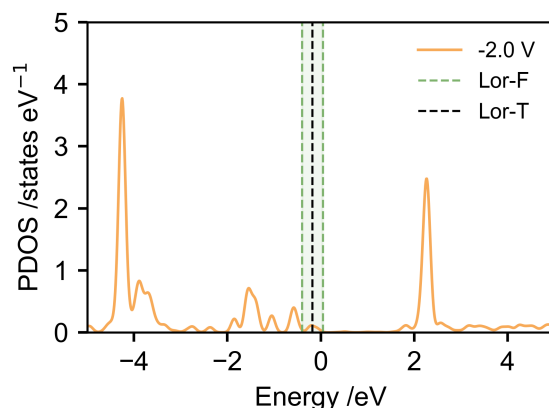


**Figure S52.** PDOS projected onto COOH s and p-states on Ni-N<sub>4</sub> SACs at -1.0 V. The peak is fitted with a Lorentzian function (Lor-F), with the integration boundary indicated by green dotted vertical lines. The corresponding integrated area is shaded in light green, while the peak maximum (Lor-T) is marked by a black dotted vertical line.

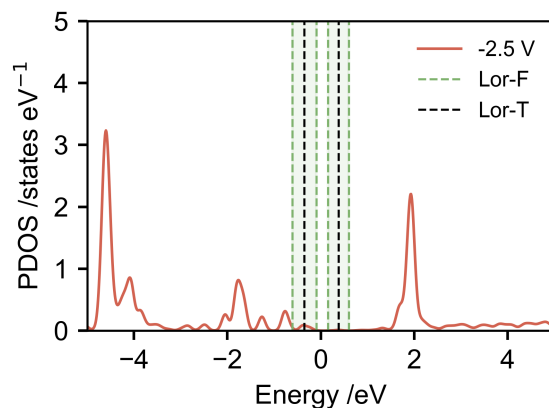




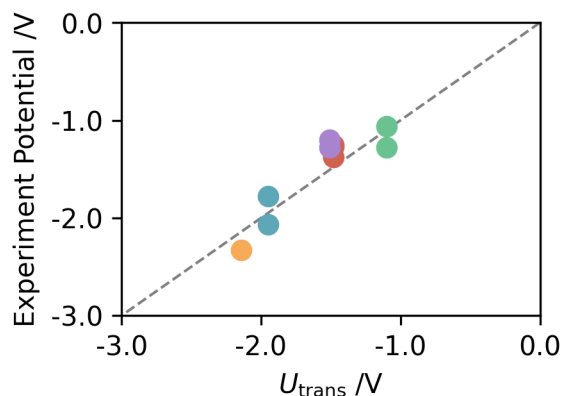
**Figure S53.** PDOS projected onto COOH s and p-states on Ni-N<sub>4</sub> SACs at -1.5 V. The peak is fitted with a Lorentzian function (Lor-F), with the integration boundary indicated by green dotted vertical lines. The corresponding integrated area is shaded in light green, while the peak maximum (Lor-T) is marked by a black dotted vertical line.



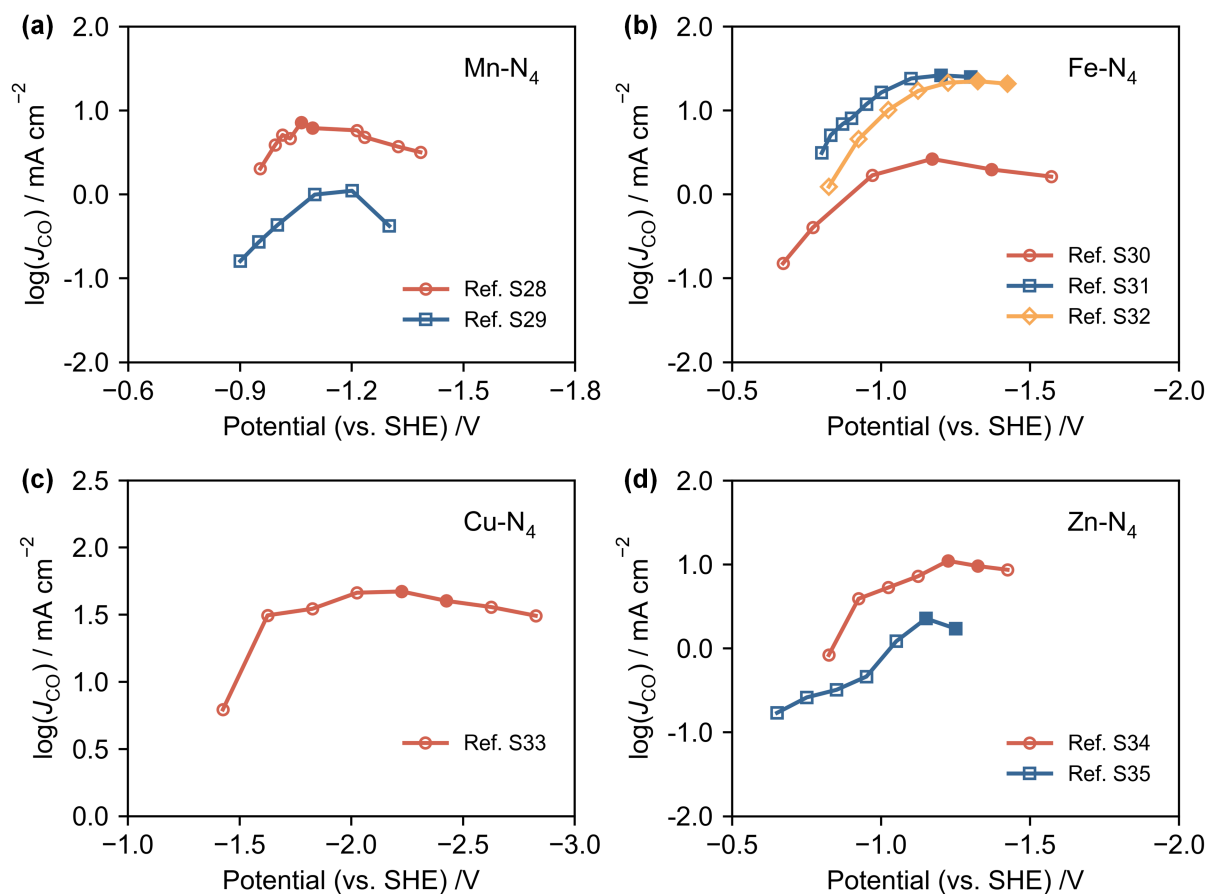
**Figure S54.** PDOS projected onto COOH s and p-states on Ni-N<sub>4</sub> SACs at -2.0 V. The peak is fitted with a Lorentzian function (Lor-F), with the integration boundary indicated by green dotted vertical lines. The corresponding integrated area is shaded in light green, while the peak maximum (Lor-T) is marked by a black dotted vertical line.



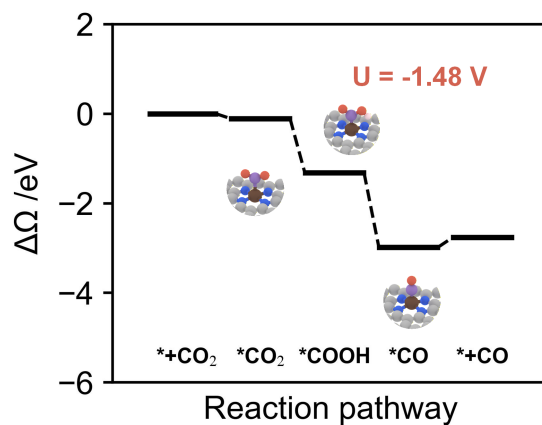
**Figure S55.** PDOS projected onto COOH s and p-states on Ni-N<sub>4</sub> SACs at -2.5 V. The peak is fitted with a Lorentzian function (Lor-F), with the integration boundary indicated by green dotted vertical lines. The corresponding integrated area is shaded in light green, while the peak maximum (Lor-T) is marked by a black dotted vertical line.



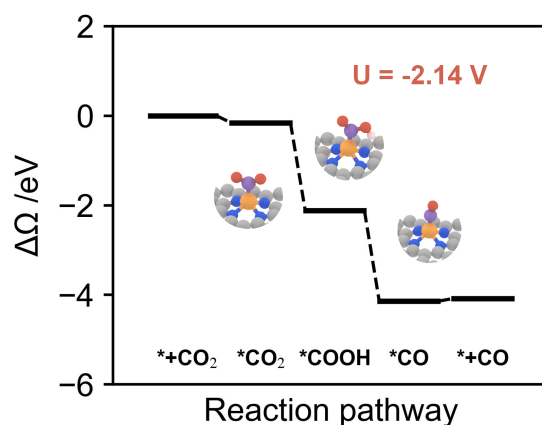
**Figure S56.** Parity plot comparing the calculated  $U_{trans}$  value with the experimental onset potential for CO yield decline across various TM-N<sub>4</sub> SACs (M=Mn, Fe, Ni, Cu, and Zn). Data points are colored by metal center: Mn with green, Fe with red, Ni with blue, Cu with orange, and Zn with purple.



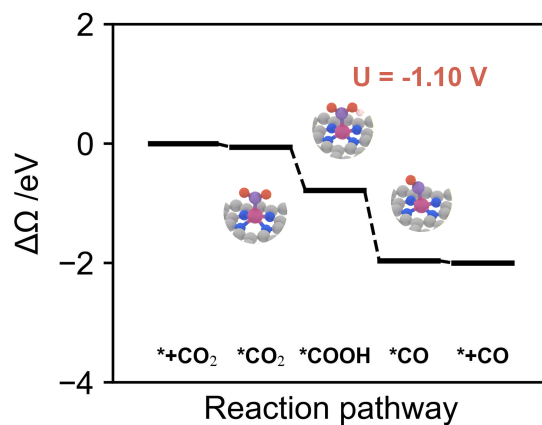
**Figure S57.** Experimental data set of CO partial current density as a function of applied potential on (a) Mn-N<sub>4</sub>,<sup>28,29</sup> (b) Fe-N<sub>4</sub>,<sup>30-32</sup> (c) Cu-N<sub>4</sub>,<sup>33</sup> and (d) Zn-N<sub>4</sub>.<sup>34,35</sup> The two solid symbols on each curve indicate the upper and lower potential limits at which the partial current density begins to decrease, and correspond to the light-colored ranges shown in Figure 6(d). All potentials are converted to values versus SHE to enable comparison across different pH conditions.



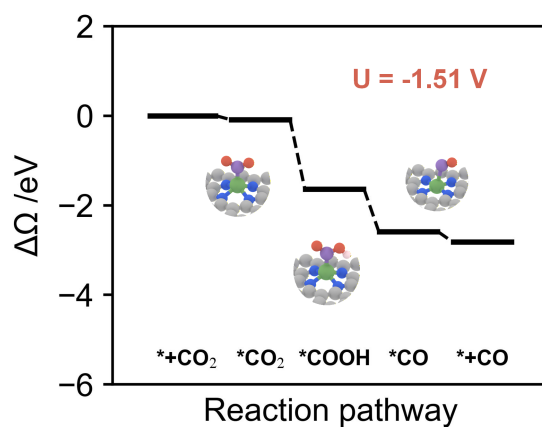
**Figure S58.** Free energy diagram of Fe-N<sub>4</sub> SACs under  $U_{trans} = -1.48$  V vs. SHE. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Fe atoms are shown in blue, red, pink, and brown, respectively.



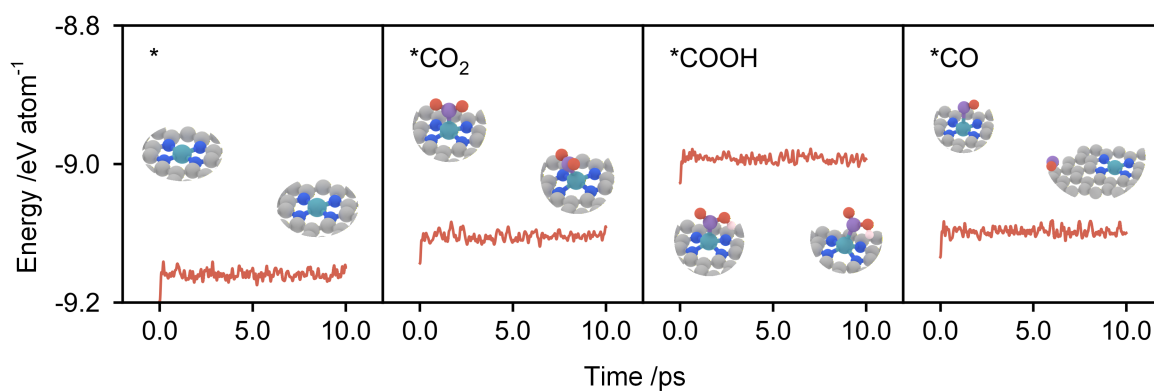
**Figure S59.** Free energy diagram of Cu-N<sub>4</sub> SACs under  $U_{trans} = -2.14$  V vs. SHE. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Cu atoms are shown in blue, red, pink, and orange, respectively.



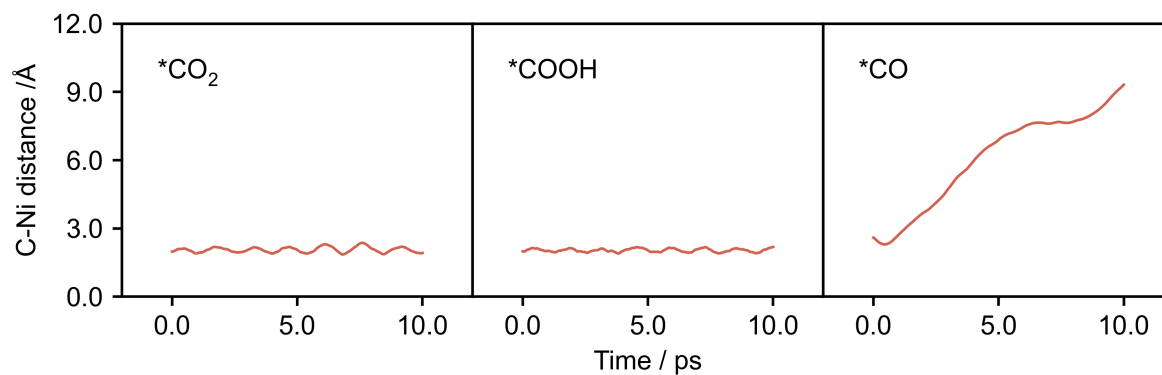
**Figure S60.** Free energy diagram of Mn-N<sub>4</sub> SACs under  $U_{trans} = -1.10$  V vs. SHE. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Mn atoms are shown in blue, red, pink, and magenta, respectively.



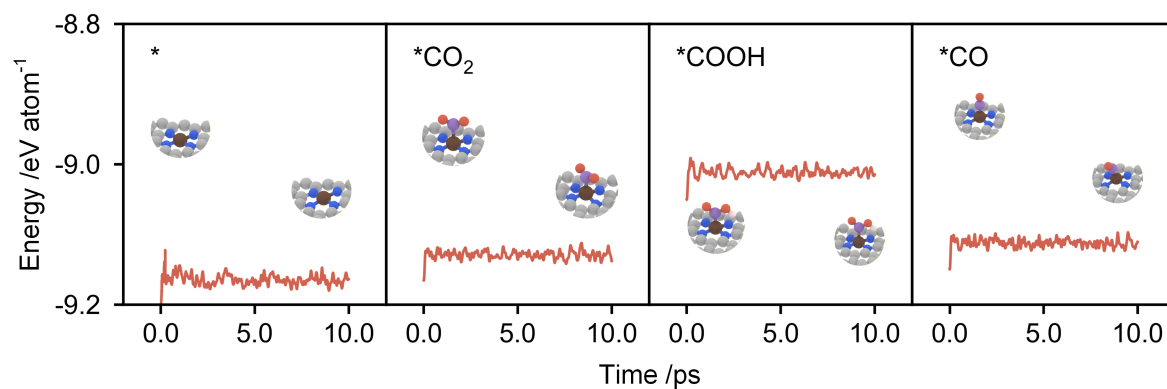
**Figure S61.** Free energy diagram of Zn-N<sub>4</sub> SACs under  $U_{trans} = -1.51$  V vs. SHE. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Zn atoms are shown in blue, red, pink, and green, respectively.



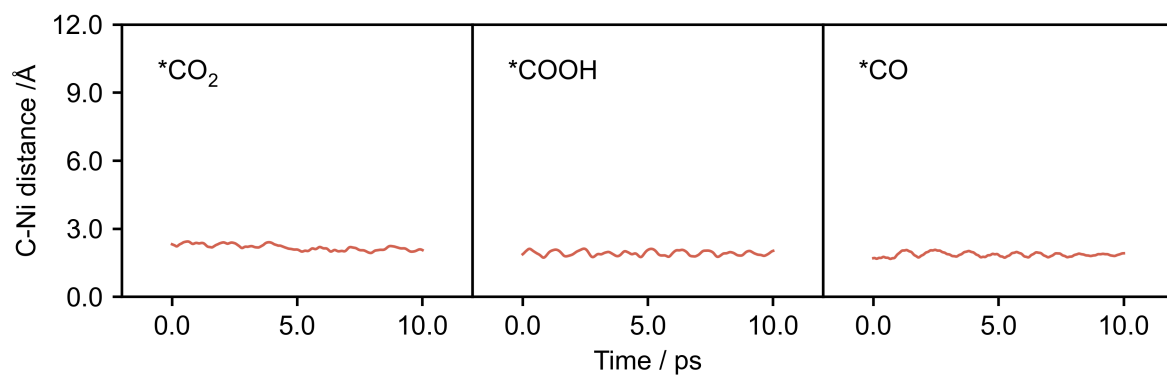
**Figure S62.** Energy evolution on Ni-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Ni atoms are shown in blue, red, pink, and cyan, respectively.



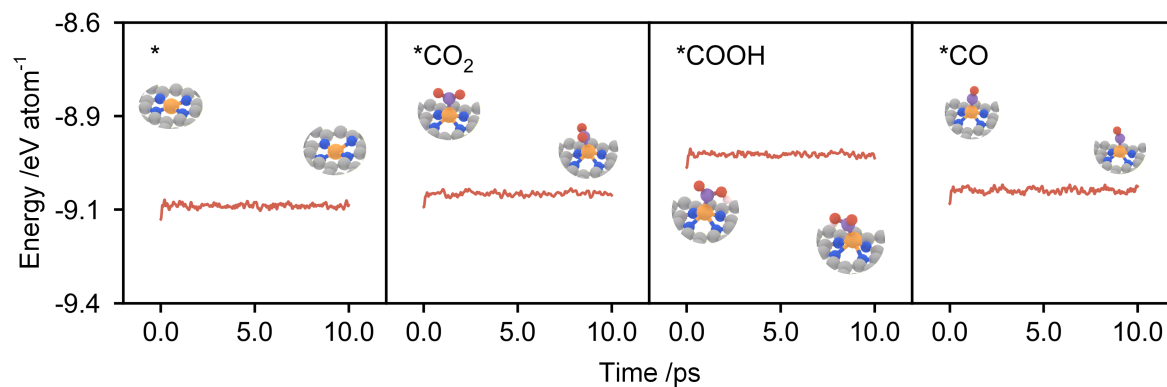
**Figure S63.** C-Ni distance variation on Ni-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K.



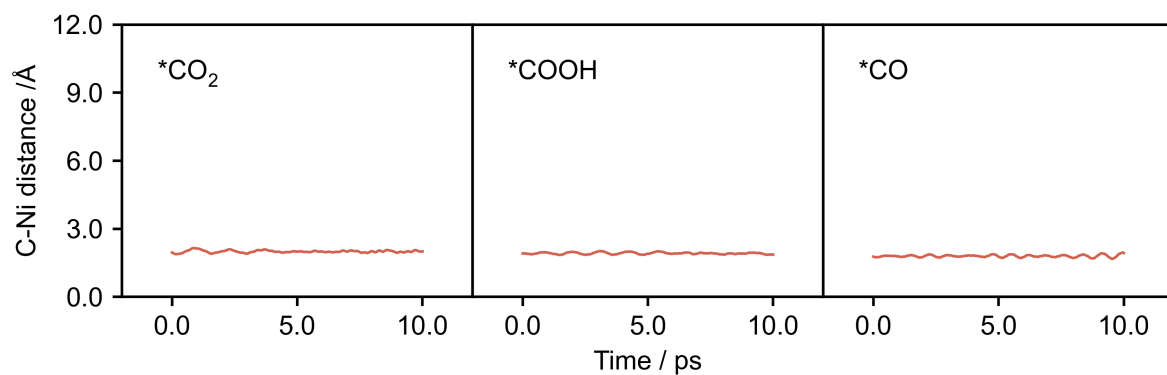
**Figure S64.** Energy evolution on Fe-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Fe atoms are shown in blue, red, pink, and brown, respectively.



**Figure S65.** C-Fe distance variation on Fe-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K.

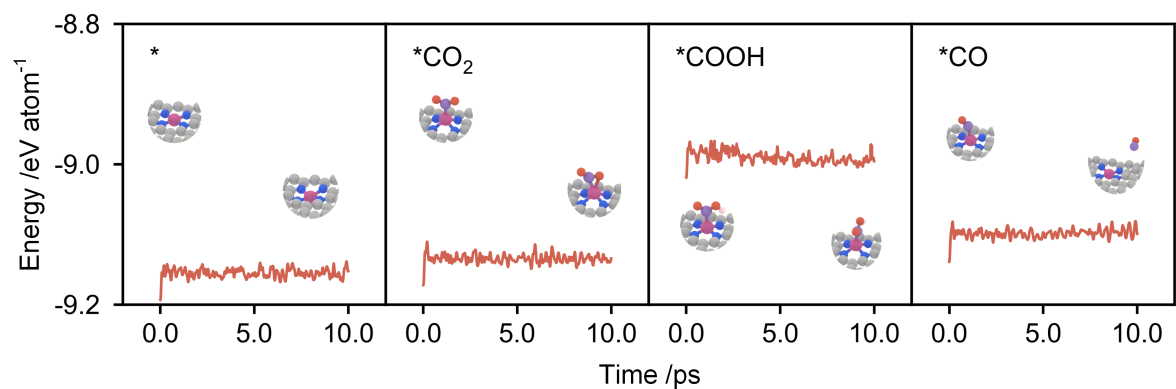


**Figure S66.** Energy evolution on Cu-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Cu atoms are shown in blue, red, pink, and orange, respectively.

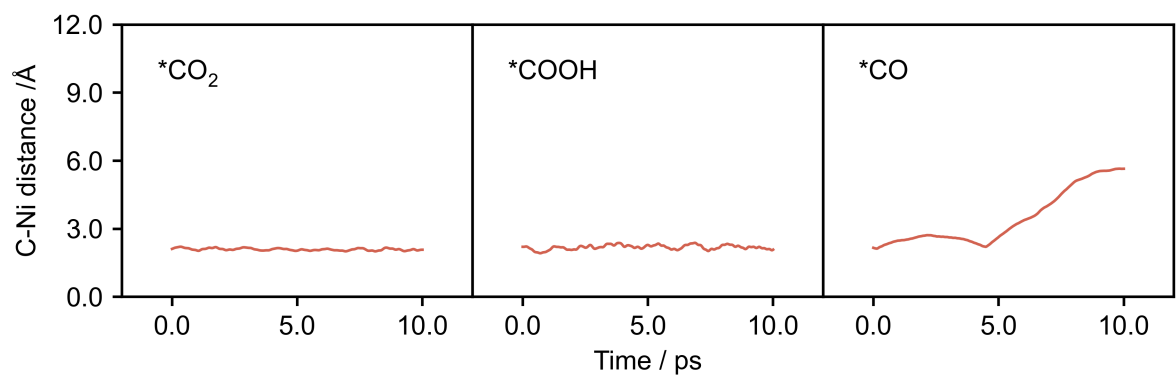


**Figure S67.** C-Cu distance variation on Cu-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K.

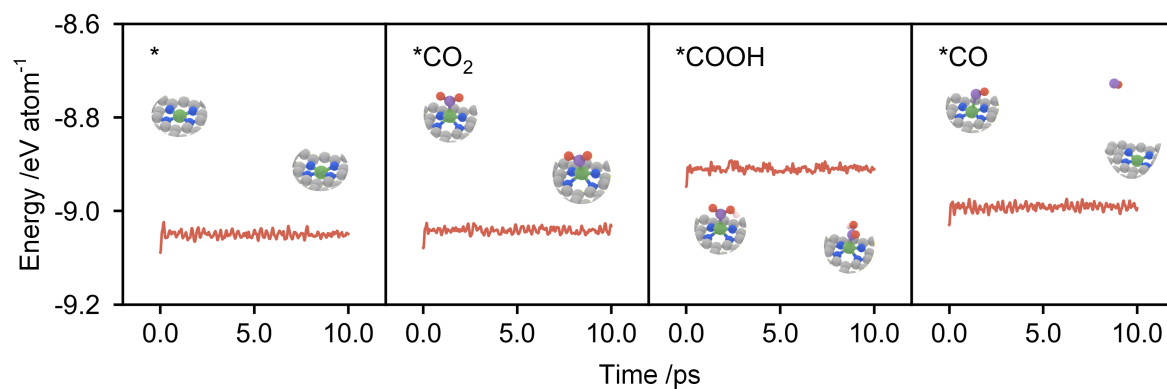




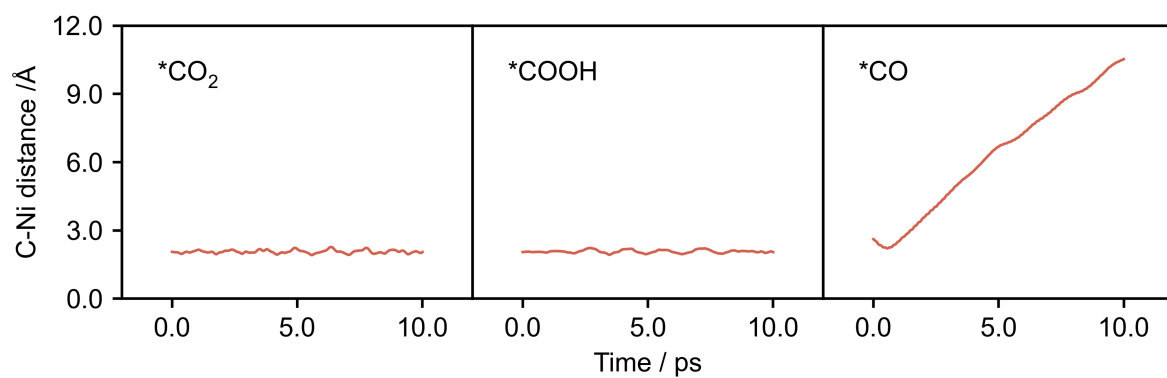
**Figure S68.** Energy evolution on Mn-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Mn atoms are shown in blue, red, pink, and magenta, respectively.



**Figure S69.** C-Mn distance variation on Mn-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K.



**Figure S70.** Energy evolution on Zn-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K. The C atoms in the graphene substrate are colored gray, while those in CO<sub>2</sub> are rendered in purple. The N, O, H, and Zn atoms are shown in blue, red, pink, and green, respectively.



**Figure S71.** C-Zn distance variation on Zn-N<sub>4</sub> SAC at  $U_{trans}$  under 300 K.

**Table S1.** The values of U parameters for DFT calculations.<sup>36,37</sup>

| 3d | Sc   | Ti   | V    | Cr   | Mn   | Fe   | Co   | Ni   | Cu   | Zn   |
|----|------|------|------|------|------|------|------|------|------|------|
| U  | 2.11 | 2.58 | 2.72 | 2.79 | 3.06 | 3.29 | 3.42 | 3.40 | 3.87 | 4.12 |

**Table S2.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from chemisorption at -1.5 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -1.5 | 0.00            | 0.96  | -469.69    | chemisorption   | chemisorption |
|      | 1.00            | 0.00  | -469.96    | chemisorption   | physisorption |
|      | 2.00            | 0.00  | -469.96    | chemisorption   | physisorption |
|      | 3.00            | 0.00  | -469.96    | chemisorption   | physisorption |
|      | 4.00            | 0.97  | -469.69    | chemisorption   | chemisorption |
|      | 5.00            | 0.00  | -469.96    | chemisorption   | physisorption |

**Table S3.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from physisorption at -1.5 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -1.5 | 0.00            | 0.00  | -469.96    | physisorption   | physisorption |
|      | 1.00            | 0.00  | -469.96    | physisorption   | physisorption |
|      | 2.00            | 0.00  | -469.96    | physisorption   | physisorption |
|      | 3.00            | 0.00  | -469.96    | physisorption   | physisorption |
|      | 4.00            | 0.00  | -469.96    | physisorption   | physisorption |
|      | 5.00            | 0.00  | -469.96    | physisorption   | physisorption |

**Table S4.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from chemisorption at -2.0 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -2.0 | 0.00            | -1.04 | -470.58    | chemisorption   | chemisorption |
|      | 1.00            | 0.00  | -470.55    | chemisorption   | physisorption |
|      | 2.00            | 0.00  | -470.55    | chemisorption   | physisorption |
|      | 3.00            | 1.04  | -470.58    | chemisorption   | chemisorption |
|      | 4.00            | 1.04  | -470.58    | chemisorption   | chemisorption |
|      | 5.00            | 0.00  | -470.55    | chemisorption   | physisorption |

**Table S5.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from physisorption at -2.0 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -2.0 | 0.00            | 0.00  | -470.55    | physisorption   | physisorption |
|      | 1.00            | 0.00  | -470.55    | physisorption   | physisorption |
|      | 2.00            | 0.00  | -470.55    | physisorption   | physisorption |
|      | 3.00            | 0.00  | -470.55    | physisorption   | physisorption |
|      | 4.00            | 0.00  | -470.55    | physisorption   | physisorption |
|      | 5.00            | 0.00  | -470.55    | physisorption   | physisorption |

**Table S6.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from chemisorption at -2.5 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -2.5 | 0.00            | -0.25 | -471.45    | chemisorption   | chemisorption |
|      | 1.00            | -0.24 | -471.45    | chemisorption   | chemisorption |
|      | 2.00            | 0.22  | -471.45    | chemisorption   | chemisorption |
|      | 3.00            | 1.06  | -471.83    | chemisorption   | chemisorption |
|      | 4.00            | 1.05  | -471.83    | chemisorption   | chemisorption |
|      | 5.00            | -1.06 | -471.83    | chemisorption   | chemisorption |

**Table S7.** Spin initialization results for CO<sub>2</sub> adsorption on Ni-N<sub>4</sub> SAC starting from physisorption at -2.5 V.

| U /V | Magnetic moment |       | Energy /eV | Adsorption Mode |               |
|------|-----------------|-------|------------|-----------------|---------------|
|      | Initial         | Final |            | Initial         | Final         |
| -2.5 | 0               | 0.00  | -471.50    | physisorption   | physisorption |
|      | 1               | 0.00  | -471.50    | physisorption   | physisorption |
|      | 2               | 0.00  | -471.50    | physisorption   | physisorption |
|      | 3               | 0.00  | -471.50    | physisorption   | physisorption |
|      | 4               | 0.00  | -471.50    | physisorption   | physisorption |
|      | 5               | 0.00  | -471.50    | physisorption   | physisorption |

**Table S8.** OMC-constrained energies (eV) of NiN<sub>4</sub>-SAC with chemisorbed (chem) and physisorbed (phys) CO<sub>2</sub> at applied potentials of -1.5, -2.0, and -2.5 V. Five distinct prescribed Ni 3d-orbital occupation patterns were examined, comprising one low-spin configuration (LS) and four high-spin configurations (HS-1 to HS-4). The lowest-energy configuration at each condition is highlighted in bold.

|      | -1.5 V         |                | -2.0 V         |                | -2.5 V         |                |
|------|----------------|----------------|----------------|----------------|----------------|----------------|
|      | chem           | phys           | chem           | phys           | chem           | phys           |
| LS   | -475.51        | <b>-474.16</b> | -477.14        | <b>-476.10</b> | -478.94        | <b>-477.64</b> |
| HS-1 | -475.46        | -472.49        | -477.30        | -474.62        | -479.12        | -476.22        |
| HS-2 | -475.41        | -472.99        | -477.13        | -474.98        | -478.83        | -476.61        |
| HS-3 | -475.54        | -473.34        | -477.28        | -475.46        | -479.12        | -477.13        |
| HS-4 | <b>-475.59</b> | -472.57        | <b>-477.34</b> | -474.65        | <b>-479.18</b> | -476.27        |

**Note.** For chemisorbed CO<sub>2</sub>, HS-4 is consistently the lowest-energy OMC configuration at all three examined potentials, whereas the LS configuration is consistently lowest in energy for physisorbed CO<sub>2</sub>. For each condition, the lowest-energy OMC solution was subsequently used as the initial state for a fully unconstrained optimization after removal of the occupation constraint. These unconstrained calculations recovered the same electronic states as those obtained in the original calculations, supporting the robustness of the identified states with respect to the initial Ni -orbital occupation.

**Table S9.** The values of  $U_{trans}$  in V for 3d TM-N<sub>4</sub> SACs.

| TM          | Sc    | Ti    | V     | Cr    | Mn    | Fe    | Co    | Ni    | Cu    | Zn    |
|-------------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|
| $U_{trans}$ | -1.58 | -0.69 | -0.35 | -1.21 | -1.10 | -1.48 | -1.02 | -1.95 | -2.14 | -1.51 |

**Table S10.** Surface energy of seven low-index Hg facets.

| Hg facet | $E_{cleave}$ (eV/Å <sup>2</sup> ) | $E_{relax}$ (eV/Å <sup>2</sup> ) | $E_{sur}$ (eV/Å <sup>2</sup> ) |
|----------|-----------------------------------|----------------------------------|--------------------------------|
| (100)    | 0.028                             | -0.010                           | 0.018                          |
| (010)    | 0.030                             | -0.006                           | 0.023                          |
| (001)    | 0.029                             | -0.009                           | 0.020                          |
| (110)    | 0.030                             | -0.001                           | 0.029                          |
| (101)    | 0.025                             | -0.001                           | 0.024                          |
| (011)    | 0.029                             | -0.008                           | 0.022                          |
| (111)    | 0.029                             | -0.007                           | 0.022                          |

**Table S11.** Two-dimensional (2D) SISSO model.

| Fitted data       | 2D SISSO model                                                                                                                                                                                        |
|-------------------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Full-data fitting | $U_{trans} = -0.47 * \ln \left( \left  E_{db} - E_{x^2-y^2_s} \right  - \left  E_{yz_s} - E_{z^2_s} \right  \right) - 0.00020 * \frac{E_{xz_s}^2 * E_{coh_b}}{R_d - E_{xz_s} + E_{x^2-y^2_s}} - 1.56$ |

**Table S12.** One-dimensional (1D) SISSO model obtained with leave-one-out cross-validation (LOOCV).

| Leaved TM | 1D SISSO model resulted from the LOOCV                                                                            |
|-----------|-------------------------------------------------------------------------------------------------------------------|
| Sc        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.58$  |
| Ti        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.59$  |
| V         | $U_{trans} = -1.59 * \sqrt[3]{ E_{db} - E_{x^2-y^2_s}  -  E_{yz_s} - E_{z^2_s} } + 0.06$                          |
| Cr        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.58$  |
| Mn        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.58$  |
| Fe        | $U_{trans} = -0.49 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.59$  |
| Co        | $U_{trans} = 0.44 * \left[ (E_{db} - E_{xy_s}) - E_{z^2_s} \right] * \frac{R_s * N_{x^2-y^2_s}}{E_{xy_s}} - 0.36$ |
| Ni        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.59$  |
| Cu        | $U_{trans} = -0.46 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.55$  |
| Zn        | $U_{trans} = -0.48 * \ln \left( \left  (E_{db} - E_{x^2-y^2_s}) -  E_{yz_s} - E_{z^2_s}  \right  \right) - 1.59$  |

**Table S13.** 2D SISSO model obtained with LOOCV.

| Leaved TM | 2D SISSO model resulted from the LOOCV                                                                                                                                                                                                                            |
|-----------|-------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------------|
| Sc        | $U_{trans} = -0.48 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) + 0.47 * \frac{\left  E_{yz_s} / E_{xy_s} - N_{x^2-y^2_s} / N_{xy_s} \right }{E_{ba} * R_s} - 1.70$                            |
| Ti        | $U_{trans} = -0.48 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) - 0.04 * \frac{\left  E_{yz_s} - E_{z^2_s} \right }{E_{coh_b} / E_{F_s} - E_{z^2_s} / E_{xy_s}} - 1.56$                        |
| V         | $U_{trans} = -1.60 * \sqrt[3]{\left  E_{db} - E_{x^2-y^2_s} \right  - \left  E_{yz_s} - E_{z^2_s} \right } - 0.07 * \left  E_{xy_s} - 2 * E_{xz_s} \right  - \left  E_{xz_s} - 2 * E_{x^2-y^2_s} \right  - 0.03$                                                  |
| Cr        | $U_{trans} = -0.47 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) - 0.15 * \frac{(E_{yz_s} - E_{z^2_s}) / (N_{xy_s} - N_{yz_s})}{\left  E_{db} - E_{coh_b} \right } - 1.57$                      |
| Mn        | $U_{trans} = -0.47 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) + 0.00012 * \frac{E_{coh_b} * N_{yz_s}}{\left  N_{yz_s} - N_{xz_s} \right } * (E_{1a} + E_{x^2-y^2_s}) - 1.51$                 |
| Fe        | $U_{trans} = -0.48 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) + 0.06 * \frac{(E_{yz_s} - E_{z^2_s}) * E_{x^2-y^2_s} / N_{yz_s}}{E_{coh_b} - E_{F_s}} - 1.57$                                 |
| Co        | $U_{trans} = 0.44 * \left[ \left( E_{db} - E_{xy_s} \right) - E_{z^2_s} \right] * \frac{R_s * N_{x^2-y^2}}{E_{xy}} - 0.0056 * \frac{E_{ba} + E_{coh_b} + E_{F_s}}{M / E_{1a}^3} - 0.56$                                                                           |
| Ni        | $U_{trans} = -0.48 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) - 0.0057 * E_{ba} * E_{coh_b} * N_{z^2_s} * \ln \left( \left  E_{yz_s} - E_{xz_s} \right  \right) - 1.52$                      |
| Cu        | $U_{trans} = -0.45 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) + 0.38 * \frac{N_{xy_s} * E_{xz_s} / E_{yz_s}}{N_{s+d} - 2 * N_{xz_s}} - 1.64$                                                 |
| Zn        | $U_{trans} = -0.48 * \ln \left( \left  \left( E_{db} - E_{x^2-y^2_s} \right) - \left  E_{yz_s} - E_{z^2_s} \right  \right  \right) - 0.061 * \left  \frac{\left  E_{yz_s} - E_{F_s} \right }{E_{coh_b} - E_{x^2-y^2_s}} - \frac{E_{yz_s}}{E_{ba}} \right  - 1.50$ |



**Table S14.** Held-out  $U_{\text{trans}}$  predictions for each TM-N<sub>4</sub> system obtained from 1D and 2D SISSO leave-one-out cross-validation (LOOCV).

| Leaved TM | DFT value | 1D prediction | 2D prediction |
|-----------|-----------|---------------|---------------|
| Sc        | -1.58     | -1.61         | -0.32         |
| Ti        | -0.69     | -0.64         | -0.63         |
| V         | -0.35     | -0.62         | -0.81         |
| Cr        | -1.21     | -1.21         | -1.15         |
| Mn        | -1.10     | -1.10         | -1.64         |
| Fe        | -1.48     | -1.55         | -1.52         |
| Co        | -1.02     | -1.32         | -1.21         |
| Ni        | -1.95     | -1.97         | -2.23         |
| Cu        | -2.14     | -2.03         | -1.98         |
| Zn        | -1.51     | -1.56         | -3.66         |

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