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The electrocatalytic CO2 reduction reaction (CO2RR) is considered as one of the most promising approaches to synthesizing carbonaceous fuels and chemicals without utilizing fossil resources. However, current technologies are still in the early phase focusing primarily on identifying optimal electrode materials and reaction conditions. Doped graphene-based materials are among the best CO2RR electrocatalysts and in the present work we have performed a computational screening study to identify suitable graphene catalysts for CO2RR to CO under alkaline conditions. Several types of modified-graphene frameworks doped with metallic and non-metallic elements were considered. After establishing thermodynamically stable electrodes, the electrochemical CO2RR to CO is studied in the alkaline media. Both concerted proton-coupled electron transfer (PCET) and decoupled proton and electron transfer (ETPT) mechanisms were considered by developing and using a generalization of the computational hydrogen electrode approach. It is established that the CO2 electro sorption and associated charge transfer along the ETPT pathway are of utmost importance and significantly impact the electrochemical thermodynamics of CO2RR. Our study suggests an exceptional performance of metal-doped nitrogen-coordinated graphene electrodes, especially 3N-coordinated graphene electrodes.

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Computational Screening of Doped Graphene Electrodes for Alkaline CO$_2$ Reduction

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Abstract

The electrocatalytic CO₂ reduction reaction (CO₂RR) is considered as one of the most promising approaches to synthesizing carbonaceous fuels and chemicals without utilizing fossil resources. However, current technologies are still in the early phase focusing primarily on identifying optimal electrode materials and reaction conditions. Doped graphene-based materials are among the best CO₂RR electrocatalysts and in the present work we have performed a computational screening study to identify suitable graphene catalysts for CO₂RR to CO under alkaline conditions. Several types of modified-graphene frameworks doped with metallic and non-metallic elements were considered. After establishing thermodynamically stable electrodes, the electrochemical CO₂RR to CO is studied in the alkaline media. Both concerted proton-coupled electron transfer (PCET) and decoupled proton and electron transfer (ETPT) mechanisms were considered by developing and using a generalization of the computational hydrogen electrode approach. It is established that the CO₂ electrosorption and associated charge transfer along the ETPT pathway are of utmost importance and significantly impact the electrochemical thermodynamics of CO₂RR. Our study suggests an exceptional performance of metal-doped nitrogen-coordinated graphene electrodes, especially 3N-coordinated graphene electrodes.
Introduction

The extensive use of fossil resources has escalated the emission of green house gases, particularly CO₂, and disrupted the atmospheric carbon balance. An appealing approach for maintaining this balance is to utilize renewable energy resources but their intermittent nature presents a serious obstacle in the energy conversion and storage applications. In this regard, converting renewable electrical energy into chemical energy through the electrochemical CO₂ reduction reaction (CO₂RR) has been identified as an efficient solution. Recently, an integrated electrocatalytic CO₂RR process has drawn appreciable attention due to its extra-ordinary features in enabling atmospheric sequestration of CO₂ followed by ambient CO₂RR to synthesize chemicals or fuels. Further flexibility is obtained by using the electrode potential and reaction conditions (pH, electrolyte) to control reaction thermodynamics and kinetics as well as activity and selectivity.

However, achieving efficient CO₂RR is a challenging task and requires optimization of the electrode material as well as the reaction conditions. There are multiple reasons for this. Firstly, CO₂ is a highly stable molecule as reflected by its high negative reduction potential (-1.90 V vs. SHE) required to drive the first-electron transfer process. To circumvent this, active electrocatalysts need to be developed, where CO₂ can be converted to several different products through sequences of complex, multistep proton-coupled electron transfer (PCET) steps. In addition, as many CO₂ derived products have similar thermodynamic stability, the developed electrocatalyst has to be selective. Controlling selectivity while retaining high activity is the primary goal in CO₂RR electrocatalysis and requires exquisite control over the complex PCET chemistry which depends sensitively on the electrode material, electrode potential, pH, and electrolyte. Therefore, optimizing the electrocatalytic performance presents a serious challenge to CO₂RR-based applications.

In the search for ideal CO₂RR catalysts, numerous metallic electrodes have been thoroughly explored experimentally and computationally. However, most of them suffer from one or several of the following shortcomings: low faradic efficiency and selectivity, high over-
potential, CO poisoning, high cost, and/or low abundance. The extended metal surfaces are also subject to the d-band center theory and intrinsic thermodynamic scaling relationships between the reaction energies of CO₂RR intermediates. These features together with the Sabatier principle set constraints on the achievable electrocatalytic performance of metallic CO₂RR catalysts and hampers the search for efficient electrode materials.²⁶,¹⁰,²²,²³

To circumvent these inherent limitations of current CO₂RR electrocatalysts, several unconventional catalyst materials have been suggested recently.²⁴–²⁸ Carbon-based electrocatalysts and in particular doped graphene sheets, are among the most promising materials and have been widely investigated as potential CO₂RR electrodes. Graphene electrocatalysts have several attractive physical properties such as high surface area, high electron mobility, high thermal conductivity, high Young’s modulus etc. Furthermore, their geometrical flexibility and electronic structure have been suggested to enable escaping the scaling relationships.²³,²⁹ While pure graphene can facilitate outer-sphere electron transfer reactions, edges or other defects are usually required for appreciable electrocatalytic activity.³⁰ Even higher activity and selectivity can be achieved by doping pristine or defected graphene with metal or non-metallic elements.³¹–³³

Given the promising CO₂RR performance of such graphene-based materials,³¹–³³ several experimental and computational investigations have explored the origin of their electrocatalytic behaviour and to search for new electrocatalysts. Most computational studies have focused on identifying the optimal reaction energies of the electrochemical PCET steps but the piling evidence³⁴–³⁶ indicates that the non-PCET CO₂ adsorption step is limiting CO₂RR. The reason for calculations focusing on electrochemical PCET steps is that the computational hydrogen electrode (CHE) model,³⁷ in its original form can only account for PCET steps. The importance of non-PCET steps, such as CO₂ adsorption, can be highlighted by comparing two recent CO₂RR studies.³⁸,³⁹ Considering only the PCET steps, led to the conclusion that CO₂RR on a Fe₄N is thermodynamically facile and a potential as small as ~0.1 V vs. RHE is sufficient to produce COOH.³⁸ However, accounting for non-PCET steps
led to a very different conclusion as the CO$_2$ adsorption itself is the potential limiting step that has a high thermodynamic barrier of $\sim$0.9 eV.\cite{59}

In addition to considering the electrode material, it should be recognized that the electrocatalytic CO$_2$RR activity and selectivity are inherent properties of electrochemical interfaces. As the interfacial properties depend sensitively on the electrode material, the electrolyte, pH, and electrode potential,\cite{26,27} they can be used for controlling the reaction environment and the electrocatalytic CO$_2$RR performance.\cite{34,40-43} Recent studies have demonstrated that the CO$_2$ adsorption step is sensitive to these properties and it also determines the CO$_2$RR activity and selectivity.\cite{34-36} Furthermore, the faradaic efficiency of CO$_2$RR is higher in alkaline conditions where the competing hydrogen evolution reaction (HER) is suppressed. Utilizing highly alkaline conditions facilitates obtaining high current densities at lower overpotentials\cite{44} and the issue of carbonate formation can be circumvented using gas diffusion electrodes.\cite{45} However, one has to consider both bulk and local pH which may differ as H$^+$/OH$^-$ are consumed or formed at the interface resulting in a pH gradient between the electrolyte and electrode interface.\cite{46,47} Furthermore, these local pH changes are found to be sensitive to the used electrode potential and current density.\cite{48}

Given the advantages of pH control and highly alkaline conditions, it is surprising that previous computational CO$_2$RR studies have solely focused on the acidic CO$_2$RR. A crucial difference between acidic and alkaline CO$_2$RR is the proton donor: in acidic conditions, the proton is donated by the hydronium ion or some other acid, whereas, under alkaline conditions, the solvent (water) is more likely the hydrogen donor. This difference can introduce changes to the reaction mechanism: A fully coupled PCET mechanism is preferred in acidic conditions, whereas, under alkaline conditions, a decoupled transfer of an electron and a proton may become the dominant mechanism.\cite{49} In order to understand alkaline CO$_2$RR, one has to examine the possibility of decoupled electron transfer/proton transfer (ETPT) steps but this requires going beyond the original CHE\cite{37} model, which is applicable to coupled PCET reactions only. This limitation can be circumvented using more general approaches.
such as general grand canonical DFT methods\textsuperscript{50–52} and the decoupled CHE.\textsuperscript{53} While these methods are applicable to ETPT pathways as well, they are currently computationally too demanding for large scale computational screening studies and more tractable methods need to be developed.

In this study, we address the CO\textsubscript{2}RR-to-CO on several graphene electrodes in alkaline conditions and account for both PCET and ETPT pathways. To enable this, the commonly applied computational hydrogen electrode method is extended to study the decoupled ETPT reactions. On this basis a computational screening approach is developed and applied to identify promising doped graphene electrocatalysts for alkaline CO\textsubscript{2}RR. A four-level selection criteria is introduced to rank and select catalysts according to their thermodynamic stability, ability to bind and activate CO\textsubscript{2}, electrosorption properties, and theoretical limiting and overpotentials. These principles allow us to identify thermodynamically stable doped graphene electrodes with low limiting and overpotentials in alkaline environments. Our study outlines that highly exergonic CO\textsubscript{2} adsorption associated with high degree of electron transfer is detrimental for catalytic performance. We find that N-coordinated Pt and Ru-doped electrodes are promising candidates as pH universal CO\textsubscript{2}RR electrodes.

**Methods**

**Modelling of graphene sheets**

Pristine graphene is modelled using a simplified non-periodic structure with 42 carbon atoms forming a honeycomb structure with 14 benzene rings. The dangling carbon atoms at the edges of the sheet are terminated with hydrogen atoms.\textsuperscript{54} Such cluster models have been demonstrated to yield results similar to the extended, periodic graphene catalysts.\textsuperscript{55}

Pristine graphene sheets are chemically inert, but their reactivity can be tuned with dopants and defects. The single vacancy is arguably the simplest point defect in graphene; however, larger point defects such as di- and tri-vacancies are also observed in experi-
ments forming after the coalescence of two or three neighboring mono-vacancies. Different vacancy and doping structures can be experimentally realized using, e.g., selective bombardment followed by ion deposition or more refined chemical synthesis. These vacancies or defects can host a variety of dopants, which we modelled by introducing foreign atom(s) into the created vacancy. These atoms include platinum group metals (Rh, Pd, Pt, and Ru), coinage metals (Ag, Au, and Cu), base metals (Al, Fe, Ni, Mo, Co, Mn, Zn, and Cr), and non-metals (B and N). Structural information for all the studied systems is provided as a supplementary data set.

We consider three different vacancy structures: single-vacancy (SV), di-vacancy (DV), and tri-vacancy (TV), by removing one, two, and three central carbon atoms, respectively. Three SV systems are investigated namely, M\textsubscript{SV}, M\textsubscript{2SV}, and MPt\textsubscript{SV} (see Figure S1(a-c)). The M\textsubscript{SV} structure results from the deposition of a single metal on a single-vacant structure and presents the simplest doped structure. In the case of M\textsubscript{2SV} and MPt\textsubscript{SV} structures, homo- and heteroatom dimers are placed on SV as models for nucleated reaction centers. We also investigated an experimentally inspired M\textsubscript{22SV} structure where two neighboring single vacancies are both filled with identical atomic dopants, see Figure S1d. The M\textsubscript{DV} structure, shown in Figure S1f has a single dopant in a di-vacancy. The trapping of dopant pairs over tri-vacant surface is energetically more favourable than a single metal dopant and have been observed experimentally, and for this reason the M\textsubscript{2TV} structure is considered as well (Figure S1h).

The N-coordinated, heteroatom-doped carbon frameworks are the most experimentally and computationally studied doped graphene electrodes for oxygen reduction reaction (ORR) and CO\textsubscript{2}RR. In these N-coordinated structure, the reaction-center is modified by replacing the coordinating carbon atoms with nitrogens. Such modifications of the M\textsubscript{SV} and M\textsubscript{DV} structures lead to the M\textsubscript{3N} and M\textsubscript{4N} electrodes having either three or four N atoms (Figure S1e&g), respectively.
Figure S1: Various models of heteroatom doped graphene electrodes: a) M_SV, b) M_2_SV, c) M_Pt_SV, d) M_2.2_SV, e) M_3N, f) M_DV, g) M_4N, and h) M_2_TV. The elements carbon, nitrogen and hydrogen are in grey, blue and lavender colors, respectively. The dopant atom is a model atom in purple color. The anchoring Pt atom in M_2_SV model is presented in teal color.
DFT methods

All density functional theory (DFT)\textsuperscript{70,71} calculations were carried out using Gaussian 09 (RB.01)\textsuperscript{72} package with the help of Gauss View \textsuperscript{5} visualizer. Exchange-correlation effects were described using the B3PW91\textsuperscript{74} functional with Grimme’s D3\textsuperscript{75} dispersion corrections. The metallic atoms were treated within the effective core potential (ECP) formalism and LANL2DZ\textsuperscript{76–78} basis set, while for all other atoms (C, H, O, N, and B) the 6-31+g(d,p)\textsuperscript{79,80} basis set was used. The structures were relaxed until the maximum residual force reached below 0.02 eV Å\textsuperscript{-1}. The satisfactory performance of the adopted computational approach has been demonstrated previously for graphene\textsuperscript{54} and metallic clusters.\textsuperscript{81–83}

The spin-inversion is an important characteristic of metal-modified graphene structures and, therefore, spin-unrestricted DFT was used and a careful investigation of spin multiplicities was necessary to locate the lowest energy spin states. To ensure the correct spin-multiplicity, single point energies at different spin multiplicities were calculated. The magnetic moment and most stable spin multiplicity of the considered graphene frameworks can be found in the Supplementary Table S1. Note that the formation and binding free energy calculations were performed using the most stable spin state structures and their energetics.

Vibrational frequency calculations were performed for all optimized structures to confirm that they are true minima. The vibrational frequencies were computed to determine the vibrational entropy and zero-point energy contributions in the thermodynamics of CO\textsubscript{2}RR. The charge analysis was based on the Mulliken scheme,\textsuperscript{84} which is assumed to be accurate enough for the comparison of similar models and similar basis sets.

Computation of catalyst stability

Electrode stability is a prerequisite to maintain catalytic activity for extended operation time.\textsuperscript{85–87} In doped graphene electrodes, the deactivation is thought to take place through dopant dissolution.\textsuperscript{88} The dissolution will result in the formation of a graphene vacancy, while the dissolved atoms will likely form metallic nanoparticles or other stable products. Hence,
the thermodynamic stability of the studied catalysts was evaluated using the formation free energy \((G_{FE})\). The formation free energy is referenced against the pristine graphene and cohesive energy of the dopants using:

\[
G_{FE} = 1/N [G_{MGr} - (N \times G_M + N \times G_{vacant Gr}) + N \times G_{coh}] \tag{1}
\]

where \(N\) is the number of dopant atoms, \(G_{MGr}\) is the free energy of the doped graphene electrode, \(G_M\) is the free energy of the metal atom, \(G_{vacant Gr}\) is the free energy of the vacant graphene, and \(G_{coh}\) is the cohesive energy of the dopant(s).\textsuperscript{89}

**Computation of reaction free energies**

The \(\text{CO}_2\) adsorption free energy \((G_{Ads})\) over the doped graphene electrodes was calculated using:

\[
G_{Ads} = [G_{MGr+CO_2} - (G_{MGr} + G_{CO_2})] \tag{2}
\]

where \(G_{MGr+CO_2}\) is the free energy of \(\text{CO}_2\) adsorbed over modified-graphene, \(G_{MGr}\) is the free energy of the bare modified-graphene, and \(G_{CO_2}\) is the free energy of gas-phase \(\text{CO}_2\).

To model alkaline conditions, we consider water as the hydrogen donor as commonly assumed for alkaline \(\text{CO}_2\)RR.\textsuperscript{89} The reaction may take place via either sequential ETPT or concerted PCET mechanism.\textsuperscript{91} In the ETPT pathway, the first ET denotes a partial charge transfer taking place during \(\text{CO}_2\) adsorption on the graphene catalyst, which is followed by further partial ET and PT. For both the sequential and concerted pathways, the elementary steps for \(\text{CO}_2\)RR to CO are:

\[
\text{CO}_2(aq) + \delta e^- + Gr \rightleftharpoons \text{CO}_2(\star)^\delta e^- \tag{3a}
\]

\[
\text{CO}_2(\star)^\delta e^- + (1 - \delta)e^- + H_2O(aq) \rightleftharpoons \text{COOH}(\star) + OH^-(aq) \tag{3b}
\]
\[ COOH(\ast) + e^- \rightleftharpoons CO(\ast) + OH^- (aq) \]  
\[ CO(\ast) + \rightleftharpoons CO(aq) + Gr \]

where \( Gr \) (also referred as "\( \ast \)"") is the graphene catalyst and \( \delta \) denotes the partial charge. When equations (3a) and (3b) are separated, the mechanism is sequential (ETPT) whereas if they are summed the PCET mechanism is followed.

To compute the electrochemical CO\(_2\)RR thermodynamics along both the ETPT and PCET pathways in alkaline conditions, the CHE method was extended to include partial charge transfer and ETPT steps. The extension is motivated by the recent decoupled hydrogen electrode method,\(^{53}\) which combines the CHE with grand canonical DFT. We utilize a computationally more feasible approximation based on the electrosorption valency\(^{92}\) to model the partial ET taking place during CO\(_2\) adsorption to capture the potential-dependency of this step. Following this approach, reaction thermodynamics for each elementary step can be computed as:

\[ \Delta G_1 (RHE) = G(CO_2^{\delta e^-}(\ast)) - G(Gr) - G(CO_2(aq)) + \gamma U(RHE) \]  
\[ \Delta G_2 (RHE) = \Delta G_w + (1 - \gamma) U(RHE) + G(COOH(\ast)) - \frac{1}{2} G(H_2(aq)) - G(CO_2^{\delta e^-}(\ast)) \]  
\[ \Delta G_3 (RHE) = \Delta G_w + U(RHE) + G(CO(\ast)) + G(H_2O(aq)) - \frac{1}{2} G(H_2(aq)) - G(COOH(\ast)) \]  
\[ \Delta G_4 = G(CO(aq)) + G(Gr) - G(CO(\ast)) \]

A complete derivation is presented in the Supplementary Material (SM). Here \( \Delta G_w = \hat{\mu}_{H^+} + \hat{\mu}_{OH^-} - \mu_{H_2O} \) is the water dissociation free energy (0.83 eV at pH=14).\(^{93}\) Equations (4a) and (4b) are written for the ETPT pathway and when added together, the reaction free energy for the concerted PCET step is obtained, i.e., \( \Delta G_{1+2}(RHE) = \Delta G_1(RHE) + \)
\( \Delta G_2(\text{RHE}) \). \( \gamma = (\partial \Delta G^{ads}(U)/\partial U) \) is the electrosorption valency\(^{12}\) which changes the adsorption energy as \( \Delta \Delta G^{ads}(U) = \gamma \Delta U \). Note that \( \gamma \leq \delta \) and the partial charge transfer upon adsorption do not directly change the Gibbs free energy. As discussed in the SM, \( \gamma \) is a potential-dependent quantity and could be obtained from experiments or using potential-dependent grand canonical DFT\(^{51,94}\) but such data is not available for the catalysts studied here. Therefore, we assume that the electrosorption valency is independent of the potential (\( \gamma(U) \approx \gamma \)), which is a good approximation at potentials close to the reference potential but breaks down as |\( U \)\( | >> |U_{\text{ref}}| \). This is seen as unphysically large equilibrium potential values for \( \text{CO}_2 \) adsorption steps – the true upper bound for the \( \text{CO}_2 \rightarrow \text{CO}^-_2 \) should be close to its thermodynamic reduction potential of -1.9 V \text{vs. SHE}^{93}\). Here, we approximate the approximate electrosorption valency using the fitting approach\(^{12}\) which gives:

\[
\gamma \approx \delta \left[ 0.84 + 0.16 \times \exp\left( -3(\chi^{Gr} - \chi^{\text{CO}_2})^2 \right) \right] \tag{5}
\]

where \( \chi \)'s are Pauling electronegativities. \( \chi^{Gr} \approx 2.5 \) for all metal-doped graphene electrodes. \( \chi^{\text{CO}_2} \approx 1.5 \) is computed using the experimental\(^{95}\) \( \text{CO}_2 \) electron affinity and ionization energies for computing its Mulliken electronegativity.\(^{96}\) The Mulliken electronegativity is then converted to the Pauling scale using the linear correlation\(^{97}\) between the two scales.

To compare and analyze the electrochemical thermodynamics, we also define the thermodynamic equilibrium potential (\( U_{eq} \)), the thermodynamic limiting potential (\( U_L \)), and overpotential (\( \eta \))\(^{98}\) as further discussed in the SM. However, our definition will take into account the ETPT steps with partial charge transfer in terms of the electrosorption valency.

\[
\begin{align}
U_{eq}(\text{RHE}) &= \left[ \sum_i \Delta G_i(U = 0 \ \text{vs RHE}) \right] / n_{e,tot} \tag{6a}
\end{align}
\]

\[
\begin{align}
U_L(\text{ETPT}) &= -\max\{\Delta G_1(U = 0)/\gamma, \Delta G_2(U = 0)/(1 - \gamma), \Delta G_3(U = 0)\} \tag{6b}
\end{align}
\]

\[
\begin{align}
U_L(\text{PCET}) &= -\max\{\Delta G_{1+2}(U = 0), \Delta G_3(U = 0)\} \tag{6c}
\end{align}
\]
\eta_{\text{PCET/ETPT}} = |U_{eq} - U_L(\text{PCET/ETPT})| \quad (6d)

where \( n_{e,\text{tot}} = 2 \) is the total number of electrons transferred in the CO₂RR to CO.

**Results**

**Structures and stabilities**

Thermodynamic stability against dissolution is a key material property mandatory for maintaining electrocatalytic activity and therefore we first addressed the stability of our graphene model electrodes. Figure S2 summarizes the Gibbs free energies for formation, computed according to eq. (6d). Additional data on formation thermodynamics with numerical values, zero-point energy corrections, and formation enthalpies are reported in the Supplementary Tables S2-S5. We found that majority of the studied dimers (M₂SV and MPt₂SV) in single vacancies are thermodynamically unstable and these results are therefore presented and discussed solely in the SM. For other systems, the findings of Figure S2 are discussed in more detail below.

**Single and two mono-vacant graphene**

The MₐSV graphenes are the simplest doped graphene structures (see Figure S1a). Calculations showed that all metal atoms exhibit slight protrusion out of the graphene plane upon bonding with the dangling carbon atoms, and the vertical distance between a metal atom and graphene plane varies from 0.73 Å to 1.19 Å in good agreement with previous computational studies. About half of the MₐSV systems are thermodynamically stable as can be seen from Figure S2. The free energy of formation ranges from -0.19 to -6.47 eV; however, doping with coinage metals and a few of base and platinum group metals is thermodynamically unfavorable (see Supplementary Table S5). The formation free energies of B- and N-doped graphene are above -6 eV, which demonstrates their extremely strong
Figure S2: Formation free energies (eV) of various heteroatom doped graphene models. Increasing negative energetics denote stronger formation stability of dopant(s) to the vacant site(s).

interaction with the graphene single vacancy.

In the case of M\textsubscript{2}2SV, the metal dopants are also elevated out of the graphene plane similar to M\textsubscript{SV}. Almost all M\textsubscript{2}2SV systems are symmetric with the dopants occupying two vacancies. The formation free energy of stable M\textsubscript{2}2SV electrodes ranges from -0.42 eV to -5.70 eV. Doping by non-metallic B and N atoms is extremely exergonic (∼-5.5 eV). We found that, upon structural optimization, the Ag, Al, and Cu dopants spontaneously drift away from the vacancy to form dimers, therefore, they are excluded from electrochemical thermodynamics studies.

Di- and tri-vacant graphene

In the M\textsubscript{DV} graphene, dopant atoms are bound to four nearest undercoordinated C atoms and remain in the basal plane due to the large size of the double vacancy compared to the dopant’s atomic radius. The considered non-metallic elements B and N feature benzene-
like hexagons with two out of the four undercoordinated carbon atoms. According to the formation free energy analysis, all M\textsubscript{DV} graphene structures are highly stable with formation energies ranging from -1.43 eV to -5.28 eV.

The tri-vacancy of M\textsubscript{2TV} models can accommodate the dopant pair in two different orientations: (i) both dopant atoms above the tri-vacancy (Supplementary Figure S4a) and (ii) one atom above and one below the tri-vacancy (Supplementary Figure S4b). We found that the latter geometry is more stable (see Supplementary Figure S4c) and was selected for further studies. In the M\textsubscript{2TV} structure, the dopant atoms are bound to the three nearest undercoordinated carbon atoms. Non-metallic B and N dimers break down during structural optimization to form benzene-like structures, and the resulting structures mimic mono-vacant graphenes. The computed formation free energies show that non-metallic dopants in the M\textsubscript{2TV} structure are highly stable, while metallic M\textsubscript{2TV} electrodes are at best modestly stable, and Ag-, Au-, Cr-, Mo-, and Ru-doped graphenes are unstable.

**N-coordinated graphene**

All the optimized M\textsubscript{3N} and M\textsubscript{4N} structures are highly symmetric and show no buckling behaviour. We find that the average M-N bond distances along with other geometrical features of both N-coordinated structures are similar to their carbon coordinated counterparts (M\textsubscript{SV} and M\textsubscript{DV}).

Our calculations suggest that the incorporation of three nitrogen atoms enhances the dopant’s stability as can be inferred from the formation free energies ranging from -1.22 eV to -3.28 eV, which are more exergonic than their M\textsubscript{SV} counterparts. The formation free energies of M\textsubscript{4N} structures vary from -1.84 eV to -2.99 eV and are comparable to the values computed for M\textsubscript{DV} models. However, it is evident that the non-metallic dopants prefer 4C-coordination as their formation free energies (see Figure S2) are much more exergonic than in the 4N-coordination environment. Therefore, the 4N-coordination environment does not enhance the stability of metallic dopants compared to 4C-coordination in agreement with previous computational results.
In general, the geometric and energetic stabilities of modified-graphene sheets depend strongly on the dopant and vacancy but some overall trends are observed. The Ag-, Au-, Cr-, and Mo-doped carbon-coordinated graphene structures are always unstable irrespective of the type of vacancy. Dopants in 3N- and 4N-environments are highly stable, which is in line with previous studies.  

**CO₂ Adsorption**

As discussed in the Introduction, CO₂ adsorption and activation are crucial steps for CO₂RR in alkaline conditions as the adsorption is often thermodynamically unfavorable and limits CO₂RR activity. Furthermore, (partial) charge transfer during CO₂ adsorption may take place and this process is sensitive to the electrode potential but independent of solution pH. CO₂ may also be activated upon adsorption, which is seen as the deviation of the O–C–O angle from 180°. Under alkaline conditions, where only weak proton donors (water) are present, the CO₂ adsorption and an accompanied ET step are important contrary to pure PCET steps. Therefore, we closely monitor the CO₂ adsorption geometry and energy over all of the considered electrodes, regardless of electrode stability. Figure S3 displays CO₂ binding geometries on the stable M_SV, M₂ SV, M_3N, M_DV, and M_4N electrodes whereas binding geometries on stable M₂ SV, MPt SV, and M₂ TV structures are illustrated in Supplementary Figure S5. Electronic structure information such as magnetic moments and stable spin multiplicities are supplied in Supplementary Table S6 for each system, and numerical values for adsorption energies, enthalpies, and free energies are provided in the Supplementary Tables S7-S10.

Among the M_SV electrodes, CO₂ adsorption is exergonic only on Fe_SV (-0.12 eV). In this case, CO₂ remains linear upon adsorption (see Figure S3a) and the oxygen atom interacts weakly with the metal site having Fe–O distance 2.16 Å and small electron transfer from CO₂ (0.22e). A similar pattern is observed for the M_DV electrodes as well. The CO₂ adsorption is exergonic only on Fe_DV (see Figure S3d) with similar binding configuration.
Figure S3: The optimized binding geometries of CO$_2$ over considered electrodes: a) Fe$_x$SV, b) Mn$_{2.2}$SV, c) Mo$_{3}$N, d) Fe$_x$DV, and e) Mo$_{4}$N. The elements carbon, oxygen, and nitrogen are in grey, red, and blue colors, respectively.

and free energy as observed for Fe$_x$SV.; however, the charge transfer (0.47e) from CO$_2$ is rather high compared to Fe$_x$SV. On the B- and N-doped SV sheets, CO$_2$ merely physisorbs as seen from the long B-C and N-C distances, which are over 3.1 Å. This is similar to the CO$_2$ adsorption on the pristine graphene. The activation of CO$_2$, i.e., non-linear CO$_2$ structure, occurs only on Mn$_x$SV and Cr- and Mo-based SV and DV structures but the CO$_2$ adsorption is thermodynamically unfavorable. Note that the formation of Cr- and Mo-doped SV electrodes are thermodynamically unstable as well.

Figure S3b illustrates the adsorption geometry of CO$_2$ on Mn$_{2.2}$SV. The adsorption geometry is similar on all the CO$_2$-activating M$_2$-2SV structures. CO$_2$ adsorption is exergonic on B-, Co-, Mn-, and N-based 2SV structures with adsorption free energies varying from -0.18 eV to -0.68 eV. However, only Co$_{2.2}$SV and Mn$_{2.2}$SV are able to activate CO$_2$ and facilitate modest electron transfer to the molecule. While Fe$_2$.2SV and Ru$_2$.2SV structures can also activate CO$_2$, they exhibit thermoneutral adsorption. On the other hand, upon structural optimization, the coinage and a few base metal (Al, Ni, and Zn) dopants stem out of the vacancies and form CO$_2$-dimer complex above graphene structure, and hence these systems were excluded from further studies.

Apart from Ag- and Cu-doped M$_3$N models, the majority of M$_3$N structures exhibit promising CO$_2$ adsorption characteristics as CO$_2$ both adsorbs and becomes activated with
the O–C–O angle varying between 127.9° to 150.4°. The molecule interacts with the metal dopant via the carbon atom and one oxygen in a bidentate conformation shown in Figure S3c for the Mo_3N structure. In the case of non-metallic dopants, CO_2 favours a monodentate adsorption configuration. The free energies of adsorption range from -0.24 eV to -0.74 eV being comparable to the values found for the M_2_2SV structures. CO_2 adsorption on 4N-coordinated electrodes is surprisingly unfavorable: roughly half of the M_4N structures can activate CO_2 but only Mo_4N (see Figure S3e) exhibits exergonic adsorption free energy (-0.89 eV) with exceptionally large charge transfer (-0.67e). Similar to M_3N graphenes, CO_2 favours a bidentate adsorption geometry on Mo_4N with O–C–O angle of 130.7°. Given the experimentally proven performance of 4N catalysts, it is unexpected to observe rather high endergonic adsorption energies on these electrodes. Possible reasons for the observed weak adsorption include, e.g., the neglected axial ligands and dipolar interactions as further elucidated in the Discussion section, or the deformation of the electrode structure upon adsorption. To test the latter, we computed the deformation energy for Fe_4N in the same way as in ref. [105] but the contribution from structural deformation is very small and therefore unfavourable adsorption energies cannot be attributed to structural deformations.

**Selection criteria**

After analyzing the electrode stabilities and CO_2 adsorption, we can develop the selection criteria for identifying the most promising modified graphene CO_2RR electrocatalysts from a large pool of materials. For instance, the doping of heteroatom to the graphene electrode should be highly stable to avoid any possible dissolution. The binding of CO_2 to the electrode material should be strong enough to avoid being the limiting step at industrially relevant current densities/potentials. Furthermore, at high pH conditions, Tafel slopes approach 120 mV/dec,[44] which is indicative of electron-transfer (ET) step being the limiting step.[91] Therefore, CO_2 should be activated upon adsorption, become negatively charged, and bind strongly: these features are ranked based on O-C-O angle, negative charge transfer, and
negative $G_{ads}$ values.

To rank and identify prospective CO$_2$RR electrocatalysts, we introduce a four-level selection criteria (see the flow chart in Supplementary Figure S6). First, we screen all bare electrodes and select the ones with negative formation free energy but disregard the systems with geometric instability. The electrodes fulfilling the first criterion are subjected to CO$_2$ adsorption energy screening. Catalysts, over which the adsorption free energy is below or equal to 0.15 eV (i.e., more adsorbing) are selected. Third, after passing the screening of binding free energies, the next step is CO$_2$ activation for which we set the threshold value of 150° for O–C–O angle. Fourth, after previous three criteria, we consider the net charge transfer due to the binding of CO$_2$ to the electrode as another criteria. In this section, the systems demonstrating net charge transfer below or equal to 0.15 are selected. The upper range of 0.15 eV in the binding free energies of CO$_2$ and in the net charge transfer is considered to account for any possible number sensitivity due to the DFT methods. This is an acceptable condition considering the fact that the electronic structure results often deviate by 0.1 eV due to different DFT functionals or basis sets.

A combined plot of three key selection parameters, i.e., adsorption free energy ($G_{ads}$), O–C–O angle, and charge transfer (q) for each of the electrode categories, namely, M$_{SV}$, M$_{DV}$, M$_{2SV}$, M$_{2TV}$, M$_{3N}$, and M$_{4N}$, is supplied in Supplementary Figure S7. Based on the selection criteria, the qualified systems to study the electrochemical thermodynamics are: M$_{2SV}$ (Co, Mn, Rh, Fe, and Ru), M$_{2TV}$ (Al, Cu, and Zn), M$_{3N}$ (Al, N, Rh, Cr, Fe, Mo, Pd, Pt, and Ru), and M$_{4N}$ (Mo and Ru). Thus, a total of 19 electrodes are selected for further study. Note that none of M$_{SV}$ and M$_{DV}$ electrodes qualify the present selection criteria.

**COOH and CO binding: Scaling relations**

CO and COOH adsorption energies typically exhibit scaling relations and are therefore often taken as CO$_2$RR activity and selectivity descriptors. However, there are indicati-
that the CO/COOH scaling relations and descriptors are not valid for graphene-based electrodes. To study whether scaling relations can be established among the materials studied here, we attempt to find correlations between the CO$_2$, COOH, and CO adsorption free energies. This analysis is carried out for the M$_3$N and M$_2$-2SV electrodes only as M$_4$N and M$_2$-TV electrodes contain too few data points. The binding energies are presented in the Supplementary Table S11 and are utilized in the next section to study the electrochemical thermodynamics.

From Supplementary Figures S8 and S9, it is evident that a poor correlation exists between the binding free energies of COOH and CO$_2$ over M$_3$N and M$_2$-2SV electrodes. Similar results are observed for COOH/CO scaling relationships on both electrodes as indicated by low $R^2$ values. These poor scaling relations are in agreement with previous studies on graphene-based electrodes, which indicates that graphene electrodes may break scaling relationships making these materials an interesting class of CO$_2$RR electrocatalysts. However, it needs to be recognized that the number of materials subjected to the scaling relation studies is small and too far-reaching conclusions on breaking scaling should be avoided. Yet, it has been shown that even slight modifications to N-doped graphene electrodes lead to different scaling relations.

**Electrochemical thermodynamics**

To address the electrochemical performance of the qualified electrodes, electrochemical thermodynamics for CO$_2$ reduction to CO were computed using equations (4) and (6). While Figure S4 displays the thermodynamic profiles for selected materials with varying behavior along the PCET and ETPT pathways, the limiting potentials and overpotentials are illustrated in Figure S5. For other materials, not shown here, the potential energy surfaces are displayed in Supplementary Figure S10 and the explicit potential values are collected in Supplementary Table S12.

As displayed in Figure S4a, a large potential difference (0.69 V) between the ETPT and
Figure S4: Electrochemical thermodynamics of CO₂ reduction reaction using PCET and ETPT mechanisms over four selected electrodes: a) Pt₃N, b) Al₃N, c) Ru₂₂SV, and d) Mo₄N.
PCET pathways is observed for the Pt$_3$N catalyst. We attribute this difference to the inclusion of the CO$_2$ binding in the former mechanism. The CO$_2$ adsorption step itself is rather exergonic and associated with a modest charge transfer ($\sim$0.3 e) from the electrode. Along the PCET pathway, COOH and CO formation steps are mildly exergonic at zero potential resulting in a positive equilibrium potential. This observation suggests that PCET pathway on Pt$_3$N is nearly thermodynamically ideal and requires zero limiting potential (blue PES). On the other hand, the ETPT mechanism is far from ideal and a large negative limiting potential is required due to the highly endergonic CO$_2$ → COOH step and the significant partial charge transfer ($\sim$0.7e) in this step. CO$_2$RR thermodynamics on the Al$_3$N catalysts, shown in Figure S4b, provides an example where both the ETPT and PCET pathways attain same limiting potential. Herein, CO$_2$ adsorption energy is modestly exergonic and features insignificant charge transfer. Furthermore, CO formation is highly unfavourable compared to COOH and is therefore identified as the potential-determining step. As the reaction free energy for CO formation (see eq. 4c) is same for both PCET and ETPT pathways, the resulting thermodynamic potentials are also equal. In Figure S4c, the Ru$_2$2SV electrode is considered. CO$_2$ adsorption is almost thermoneutral at zero potential (red line) associated with a small charge transfer ($\sim$0.2e) from the electrode. The formation of COOH is identified as the limiting step owing to its high endergonicity. Altogether these factors make ETPT and PCET limiting potentials rather similar, which in turn implies that this material is a promising candidate for both ETPT and PCET pathways, i.e., for both alkaline and acid conditions. However, the CO adsorption free energy ($\sim$1 eV) on the electrode is too strong which makes it susceptible to catalyzing further reduction or poisoning. The last example, given in Figure S4d, features very different limiting potentials for the ETPT and PCET pathways on the Mo$_4$N electrode. In this case, CO$_2$ adsorbs strongly, significant charge transfer ($\sim$0.7e) to the molecule takes place, and the COOH formation is quite endergonic at zero potential (red line). Together these factors result in a large negative limiting potential along the ETPT pathway, while the PCET exhibits a fairly
modest overpotential. Similar behaviour is seen for the Mo₃N electrode as well and we conclude that the N-Mo-modified graphene catalysts are unsuitable for a ETPT mechanism but could work for the PCET pathway.

Comparison of the ETPT potential energy profiles given in Figure S4 shows CO₂ adsorption and associated charge transfer are pivotal for this mechanism to be operational but they are absent from PCET due to the assumption of simultaneous electron and proton transfer. Overall, these differences modify the reaction thermodynamics, and we observed that the charge transfer during adsorption has a profound effect on the electrocatalytic thermodynamics as manifested by the limiting potentials shown in Figures S4 and S5. We found that the slightly exergonic CO₂ adsorption is beneficial as it enables the formation of a stable CO₂-catalyst complex and prevents excessively endergonic COOH formation. Furthermore, charge transfer associated with CO₂ adsorption should be as low as possible; if the COOH formation requires only a very small degree of charge transfer, a very high reductive potential is needed to make this step thermodynamically favorable as shown in, e.g., Figure S4d. In a case where no charge transfer takes place during \(\text{CO}_2^- + \text{H}^+ \rightarrow \text{COOH}\), the COOH formation step is fully chemical and cannot be controlled by the electrode potential. The very large limiting potentials along the ETPT pathways are likely an artefact of the simple charge transfer and electrosorption model adopted herein but we believe that the model allows qualitative comparison of thermodynamics between ETPT and PCET processes.

The thermodynamic potentials are extensively used for ranking or comparing the expected performance of different catalysts, and limiting potentials and overpotentials should be close to zero for the best performing catalysts. Figure S5 presents both potentials for the PCET and ETPT pathways. For all the qualified electrodes, the overpotentials are within 0.7 V (vs. RHE) for PCET pathways. The best-performing electrodes include Ru, Rh, and Mo-doped 3N graphene and Ru and Mo-doped 4N graphene for which the limiting potentials vary from 0 to -0.52 V vs. RHE and overpotentials range from 0.06 to 0.21 V vs. RHE. For the ETPT mechanism, the best-performing electrodes contain Pd₃N, Ru₃N, Pt₃N, Ru₂.2SV,
Figure S5: Calculated theoretical limiting (0 to -2.0 V vs. RHE) and overpotential (0 to 1.5 V vs. RHE) of electrocatalytic CO\textsubscript{2}RR process via PCET and ETPT mechanisms.
and Ru$_4$N with limiting potentials between -0.48 and -0.86 V vs. RHE and overpotentials varying from 0.28 to 0.8 V vs. RHE. The limiting potentials found for the studied structures are either comparable or even smaller than those previously computed for 4N and 3N catalysts, non-metallic defected graphene, and single-atom doped metal catalysts. Overall, the ETPT mechanism leads to higher overpotentials and limiting potentials than the PCET pathway. Interestingly, we find that three of the studied materials – Ru$_3$N, Pt$_3$N, and Ru$_4$N – exhibit very promising electrochemical thermodynamics along both the ETPT and PCET pathways making these materials promising candidates for CO$_2$RR under both acid (PCET) and alkaline (ETPT) conditions.

**Discussion**

Our computational predictions show that the CO$_2$RR activity and selectivity on a given graphene-based electrode depend on the mechanism, i.e., whether the PCET or ETPT pathway is followed. For conditions favoring the PCET mechanism, the N-coordinated graphene electrodes demonstrate the best performance among the studied models. The aforementioned holds true also when ETPT is operational but this typically leads to larger limiting potentials. Pd$_3$N is an exception to this rule and is the only electrode for which a lower overpotential along the ETPT than the PCET pathway is observed. This anomaly is caused by the slightly positive CO$_2$ binding energy and minor charge transfer. In general, the coupled PCET is thermodynamically more favorable but for kinetic reasons the ETPT pathway may be preferred.

The obtained results show that the ETPT pathway is highly sensitive to the CO$_2$ adsorption energy and charge transfer. Ignoring these important features from mechanistic consideration and focusing solely on the PCET mechanism, often leads to a different potential-determining step, and underestimation of thermodynamic potentials. For example, the current and previous computational studies on Fe$_4$N show that the CO$_2$ bind-
ing itself introduces a thermodynamic barrier of \( \sim 0.9 \text{ eV} \), whereas, the PCET pathway\(^{35}\) presents a quite small (\( \sim 0.1 \text{ eV} \)) thermodynamic barrier for producing COOH. These results demonstrate that CO\(_2\) adsorption directly affects the CO\(_2\)RR thermodynamics and should therefore be considered. The adsorption process is particularly important under alkaline conditions where the coupled PCET becomes less likely, and at high current densities where mass transfer and adsorption are the limiting processes. We identified that slightly exergonic CO\(_2\) adsorption associated with minor charge transfer is a desirable feature for promising catalysts. The conclusions from a large number of studies (see Introduction) neglecting the adsorption step and focusing only on PCET steps are limited to acidic conditions or to the electrodes that cannot catalyze the ETPT pathway.

The importance of the adsorption step can be further illustrated by the widely studied Fe\(_{4N}\) electrode. Our results suggest that the Fe\(_{4N}\) electrode\(^{36,39,111}\) does not belong to the best performing CO\(_2\)RR materials. We attribute this to the thermodynamically unfavorable CO\(_2\) adsorption step which agrees with the recent finding that the adsorption step on Fe\(_{4N}\) is thermodynamically uphill even under high electrode potentials and field strengths.\(^{36}\) Therefore, CO\(_2\)RR on Fe\(_{4N}\) is limited by CO\(_2\) adsorption and mass transfer at industrially relevant current densities.\(^{46}\) Even though our decoupled pathway and CO\(_2\)RR analyses are based on a relatively simple and ideal electrosorption valency concept, the identification of CO\(_2\) adsorption as a crucial step is expected to be rather general. In particular, our approach provides a fast approach to identify a catalyst, where ET during adsorption is an important feature.

A recent joint experimental and computational work\(^{39}\) has shown that axial ligands are important in determining the CO\(_2\)RR to CO performance on M\(_{4N}\)-type materials. While the experimental results exhibit a high current density and Faradaic efficiency towards CO at applied potentials of -0.5 and -0.6 V \( \text{vs. RHE} \), the calculations predict a significant thermodynamic barrier of \( \sim 0.9 \text{ eV} \) for CO\(_2\) adsorption in agreement with our results. As the initial computational results were not in line with the experimental findings, the effect of axial
adsorption of H₂O, OH, and O was considered. While the adsorption energy was found to be independent of axial OH/O adsorption, the axially adsorbed H₂O stabilized CO₂ adsorption on Fe₄N by ~0.3 eV. Including the axial H₂O ligand in the computational Fe₄N model resulted in a better agreement with experiments as the CO₂ adsorption posed only a small (0.06 eV) thermodynamic barrier at -0.6 V vs. RHE. Furthermore, the simulated Pourbaix diagrams confirmed that Fe₄N electrode may bind axial ligands on both sides. While the kinetic role of the axial ligands was not considered for CO₂RR, the oxygen reduction reaction kinetics were shown to be very sensitive to the presence of "innocent" axial ligands.

Previous studies suggested that CO binding strength is a descriptor that determines the CO₂RR product distribution. Materials with strong CO adsorption are either poisoned or produce C₁- or C₂ species or form hydrogen via the competing HER. On the contrary, electrodes binding CO weakly yield CO as the major product due to favourable CO desorption kinetics. Apart from Al-, Cr-, and Pd-dopants, the majority of 3N-coordinated electrodes bind CO quite strongly suggesting that they might be poisoned by CO. The CO adsorption on Al₃N (ηETPT/PCET = 0.69 V) is weak and leads to facile CO desorption. Intermediate CO adsorption energies on Cr₃N and Pd₃N suggest that these two materials are promising electrocatalysts for producing C₁- or C₂ molecules; however, the former suffers from rather high limiting potential making Pd₃N the only 3N-graphene electrode suitable for further CO reduction. Apart from Ru₂-2SV, all other 2SV electrodes exhibit CO binding strength within ~0.7 eV indicating that they will primarily produce CO. The M₂-2SV electrodes show low overpotentials but feature high negative limiting potentials (above -1V) except for Ru₂-2SV, which is identified as the most promising M₂-2SV structure. Both M₄N and M₂-TV electrodes suffer from either strong CO binding or high limiting potentials, and are therefore unsuitable for CO production.
Conclusions

In this work, we have identified promising modified graphene electrodes for CO$_2$RR to CO under alkaline conditions. Robust selection criteria based on thermodynamic stability, CO$_2$ adsorption thermodynamics, and potential-dependent reaction free energies are devised and applied. The computational hydrogen electrode concept has been extended to treat decoupled PCET steps to account for the possible decoupled ETPT mechanism in alkaline conditions. Following this procedure, it is found that a high degree of partial charge transfer during CO$_2$ is detrimental to electrocatalyst performance and that moderately strong CO$_2$ adsorption energy without charge transfer leads to promising electrode materials. We have identified metal sites coordinated to three nitrogen atoms (M$_3$N) and two single vacancy metal (M$_2$-2SV) electrodes as highly promising materials for CO$_2$RR following either the coupled or decoupled pathways. N-coordinated Ru and Pt electrodes exhibit promising characteristics for both coupled and decoupled pathways making these materials interesting candidates as pH-universal CO$_2$RR electrodes and call for further experimental and computational studies.

Supplementary material

See supplementary material for the derivation of PCET and ETPT thermodynamics, and complete data of formation free energies of graphene electrodes, magnetic moments and stable spin multiplicities, binding free energies of CO$_2$ and the associated charge transfers, thermodynamic profiles, thermodynamic potential values, and scaling relationship plots. The xyz coordinates of all optimized structures are provided as a dataset and can be found on our group’s gitlab page: https://gitlab.com/compcatjyu/co2rr-on-graphene-electrodes
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Derivation of free energies for simultaneous and decoupled PCET reactions

Here thermodynamic relations used in the main paper are derived. Expression for both decoupled electron (ET)/proton transfer (PT) steps and concerted proton-coupled electron transfer (PCET) steps are developed.

The reaction mechanism and needed thermodynamic identities

We consider the following reaction steps

\[
CO_2(aq) + \delta e^- + Gr \Leftrightarrow CO_2(^*)^{\delta e^-} \quad (1a)
\]
\[
CO_2(^*)^{\delta e^-} + (1 - \delta)e^- + H_2O(aq) \Leftrightarrow COOH(^*) + OH^- (aq) \quad (1b)
\]
\[
COOH(^*) + e^- \Leftrightarrow CO(^*) + OH^- (aq) \quad (1c)
\]
Next the free energy for each step is derived. We will need the following basic thermo-
dynamic identities.

- Gibbs energy is $G = \sum_i \tilde{\mu}_i n_i$. For the proton the chemical potential is $\tilde{\mu}_{H^+} = \mu_{H^+} + \phi^S - k_B T \ln 10 \times pH$ where $\phi^S$ is the (local) electric potential in solution.

- The water dissociation energy is $K_w = \exp[-\Delta G_w/k_B T]$ with $\Delta G_w = \tilde{\mu}_{H^+} + \tilde{\mu}_{OH^-} - \mu_{H_2O}$. The water dissociation free energy is obtained from standard electrochemical tables and at pH=14 $\Delta G_w=0.83$ eV.[1]

- The absolute electrode potential in the vacuum scale is $U_{abs} = -\tilde{\mu}_e = -(\mu_e - \phi^M) = -eE_F$ where $\phi^M$ is the electrostatic potential in the electrode. Reference against the standard hydrogen electrode (SHE) is obtained as $U(SHE) = -\tilde{\mu}_{ABS}^{e} - (-\tilde{\mu}_{SHE}^{e}) = U_{ABS} - U_{ABS}^{SHE}$.[2,3]

- The computational hydrogen electrode (CHE)[4] is defined from the reaction

$$H^+ + e^- \rightleftharpoons 1/2H_2$$

The free energy for this reaction is $\Delta G_{CHE} = 1/2\mu_{H_2} - \tilde{\mu}_{e^-} - \tilde{\mu}_{H^+} = 1/2\mu_{H_2} - \tilde{\mu}_{e^-}^0 + \Delta \phi - \mu_{H^+}^0 + k_B T \ln 10 \times pH = +\Delta \phi + k_B T \ln 10 \times pH$ where $1/2\mu_{H_2} - \tilde{\mu}_{e^-}^0 - \mu_{H^+}^0 = 0$ by definition at $U = 0$ vs. SHE and pH=0. With these definitions the reaction energy on the SHE/CHE scale becomes $\Delta G(SHE) = U(SHE) + k_B T \ln 10 \times pH$

- The SHE scale is converted to the RHE scale by subtracting the pH term

**Step 1: Electrosorption of CO$_2$**

The reaction free energy of the CO$_2$ adsorption in step (la) is formally
\[ \Delta G_1 = \tilde{\mu}_{CO_2} - G(Gr) - \mu_{CO_2(g)} - \delta \tilde{\mu}_e \]  

(3)

However, it can be shown\textsuperscript{5} that dividing the charge between the catalyst and the adsorbate is superficial as the charge transfer depends on the utilized model. In particular, the thermodynamics from the Gibbs adsorption equation remain unchanged on whether the adsorbate and catalysts are treated as a single constituent or as separate species.\textsuperscript{5} Therefore the species’ surface excess free energy determining the free energy change is independent on whether or not charge transfer takes place as only the total surface charge of the electrode and the adsorbed species can be determined.

To account for the effect of the electrode potential on the adsorption energy, a recent study\textsuperscript{6} utilized a dipolar model for CO\textsubscript{2} and adsorption was taken to depend on the electrode potential as \( \Delta G(U)_{CO_2} = \Delta G_0 + \nu \vec{E}(U) \right\vert - \alpha \right\vert a(\vec{E}(U))^2 \) where \( \Delta G_0 \) is the reference adsorption energy at \( U = 0 \) vs SHE, \( \vec{E}(U) \) is the electric field felt by the adsorbed CO\textsubscript{2} as a function of the potential, \( \nu \) is the dipole moment, and \( \alpha \) is the polarizability. In this model, the \( \Delta G(U)_{CO_2} \) has a linear dependence on \( U \) with a slope depending on the electrode material under the assumptions used in Ref. \textsuperscript{6}. Another thermodynamically well-defined way to include the potential dependency in the adsorption energy is obtained through the use of the electrosorption valency,\textsuperscript{5} \( \gamma(U) \). Unlike Schmickler and Guidelli,\textsuperscript{5} we have included the potential dependence in the definition of the electrosorption valency because the (CO\textsubscript{2}) adsorption energy may depend non-linearly on the electrode potential. Including the potential dependency in the electrosorption valency gives

\[ \gamma(U) = \left( \frac{\partial \Delta G_{\text{ads}}(U)}{\partial U} \right)^\Gamma_i \]  

(4)

where \( \Gamma_i \) denotes the surface excess of all species. Using the CO\textsubscript{2} adsorption free energy at some reference potential, \( \Delta G_1(U_{\text{ref}}) \), the effect of changing the potential maybe computed using the electrosorption valency. For the ease of calculation, we assume that the
electrosorption valency is independent of the potential ($\gamma(U) \approx \gamma$) - this assumption should be valid close to the reference potential but will deteriorate for potentials $|U| >> |U_{ref}|$.

With the assumption, the adsorption energy as a function of the electrode potential is

$$\Delta G_1(U) = \Delta G_1(U_{ref}) + \gamma \times (U - U_{ref}) \quad (5)$$

The reference potential is chosen on the SHE scale and set to zero. This defines the free energy change as

$$\Delta G_1(U_{SHE}) = \Delta G_1(U(SHE) = 0) + \gamma \times U(SHE) \quad (6)$$

**Step 2: PT and partial ET**

To facilitate the use of the CHE model, step 1b is separated to three steps using a thermodynamic cycle in Fig. S1

![Figure S1: Thermodynamic cycle for step 2.](image)

The first substep is the water dissociation step and the free energy change for this steps was given in above: $\Delta G_2' = \Delta G_w$. The second substep is the hydrogen evolution step which we take on the SHE scale using the CHE model. The free energy change for this step also discussed above and results in: $\Delta G_2'' = U(SHE) + k_B T \ln 10 \times pH$. The final substep is the formation of the adsorbed carboxyl species and the free energy is formally

$$\Delta G_2''' = \mu_{COOH^{(*)}} - \frac{1}{2} \mu_{H_2} - \tilde{\mu}_{CO_2^{δe-(*)}} - \delta \tilde{\mu}_e \quad (7)$$

As discussed for Step 1, $\tilde{\mu}_{CO_2^{δe-(*)}}$ is thermodynamically indistinguishable from the $\tilde{\mu}_{CO_2^{(*)}}$ +
\[ \delta \tilde{\mu}_w. \] Therefore, we can replace the chemical potential \( \text{CO}_2(\text{\texttrade}) \) with adsorption energy at some reference potential and and account the electrode potential using the electrosorption valency discussed in relation to Step 1. This leads to

\[ \Delta G'''''_2 = \mu_{\text{COOH}(\text{\texttrade})} - \frac{1}{2} \mu_{\text{H}_2} - \mu_{\text{CO}_2(\text{\texttrade},U(SHE)=0)} - \gamma \times U(SHE) \]  

(8)

Then, the free energy change of step 2 is

\[ \begin{align*}
\Delta G_2 &= \Delta G'_2 + \Delta G''_2 + \Delta G'''''_2 \\
&= \Delta G_w + \mu_{\text{COOH}(\text{\texttrade})} + (1 - \gamma)U(SHE) + k_B T \ln 10 \times pH \\
&- \frac{1}{2} \mu_{\text{H}_2} - \mu_{\text{CO}_2(\text{\texttrade},U(SHE)=0)}
\end{align*} \]

(9)

**Steps 1+2: Concerted PCET**

If the ET and PT take place in one concerted step, the free energy change is simply

\[ \Delta G_{1+2} = \Delta G_1 + \Delta G_2 \]

\[ \begin{align*}
&= \Delta G_w + \mu_{\text{COOH}(\text{\texttrade})} + U(SHE) + k_B T \ln 10 \times pH \\
&- \frac{1}{2} \mu_{\text{H}_2} - \mu_{\text{CO}_2(\text{\texttrade},U(SHE)=0)}
\end{align*} \]

(10)

which is the same as derived from the traditional CHE model for concerted PCET, as it should be.

**Step 3: Concerted PCET**

For this step the thermodynamic cycle in Fig S2 is utilized. The addition of water on both sides of the total reaction does not affect the total thermodynamics but facilitates the use of the CHE model.
The first substep is the water dissociation reaction for which the free energy change is 
\[ \Delta G'_3 = \Delta G_w. \] The second substep is again the hydrogen evolution step which we take on the 
SHE scale and employ the CHE model. The free energy change for this step is also discussed 
in relation to Eq. 2 and yields: 
\[ \Delta G''_3 = U(SHE) + k_B T \ln 10 \times pH. \] The final substep is the 
formation of CO and the free energy change is obtained using CHE 
\[ \Delta G'''_3 = \mu_{CO(\ast)} + \mu_{H_2O} - \frac{1}{2} \mu_{H_2} - \mu_{COOH(\ast)} \] (11)

The free energy change of step 3 is then 
\[ \Delta G_3 = \Delta G'_3 + \Delta G''_3 + \Delta G'''_3 \]
\[ = \Delta G_w + U(SHE) + k_B T \ln 10 \times pH + \mu_{CO(\ast)} + \mu_{H_2O} - \frac{1}{2} \mu_{H_2} - \mu_{COOH(\ast)} \] (12)

**Theoretical equilibrium, limiting, and overpotential**

The theoretical equilibrium potential is the potential at which initial and final states have 
equal free energies. The limiting potential is the applied electrode potential at which all en-
ergy steps are either exergonic or thermoneutral. The overpotential is a measure of the extra 
potential needed compared to the equilibrium potential and is calculated as the difference 
between equilibrium and limiting potentials.
Figure S3: Various models of heteroatom doped graphene electrodes: a) M_{SV}, b) M_{2 SV}, c) MPt_{SV}, d) M_{2 SV}, e) M_{3 N}, f) M_{DV}, g) M_{4 N}, and h) M_{2 TV}. The elements carbon, nitrogen and hydrogen are in grey, blue and lavender colors, respectively. The dopant atom is a model atom in purple color. The anchoring Pt atom in MPt_{SV} model is presented in teal color.

**Formation of M_{2 SV} and MPt_{SV} models**

In the dimetallic (M_{2 SV}) models, heteroatom dimers occupies over a mono-vacant graphene site (see Figure S3). Similar to M_{2 SV} models, the bi-metallic MPt_{SV} electrodes (see Figure S3) are based on the anchoring of Pt atom on the metal site of M_{SV} models. In general, both the M_{2 SV} and MPt_{SV} electrodes are highly unstable and only three systems (B, Mn, and N dimers) are stable. Experimental evidence for the existence of MPt_{SV} and M_{2 SV} electrodes could not be found even though the results of a previous computational study\(^7\) suggest that the nucleation of homo- and heteroatoms over M_{SV} graphene sheets may take place. However, the absence of experimental evidence and computational results herein indicate that MPt_{SV} and M_{2 SV} are not likely to exist. Below, we do analyse the
Table S1: Magnetic moment (eV) and stable spin multiplicity (in the parenthesis) of heteroatom doped graphene models.

| M   | M_SV | M_3N | M_DV | M_2 SV | M_4N | M_2 TV | M_2 SV | MPt_SV |
|-----|------|------|------|--------|------|--------|--------|--------|
| Ag  | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| Al  | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| Au  | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| B   | 0.00 (2) | 0.14 (3) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| Co  | 0.00 (2) | 0.49 (3) | 0.00 (2) | 0.12 (3) | 0.00 (2) | 0.64 (3) | 1.02 (3) | 0.00 (2) |
| Cu  | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| Mn  | 0.46 (4) | 0.99 (7) | 0.76 (6) | 1.61 (5) | 0.37 (4) | 1.94 (7) | 3.44 (7) | 1.01 (4) |
| N   | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) | 0.00 (2) |
| Rh  | 0.00 (2) | 0.28 (3) | 0.00 (2) | 0.22 (3) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Cr  | 1.56 (3) | 0.00 (2) | 1.38 (3) | 0.76 (3) | 1.88 (7) | 0.07 (3) | 2.43 (3) | 1.03 (3) |
| Fe  | 0.00 (1) | 0.52 (4) | 0.43 (3) | 0.37 (3) | 0.84 (5) | 1.76 (5) | 1.99 (5) | 0.58 (3) |
| Mo  | 0.81 (3) | 0.00 (2) | 0.30 (3) | 0.00 (1) | 0.58 (5) | 0.00 (1) | 0.73 (3) | 0.52 (3) |
| Ni  | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) |
| Pd  | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) |
| Pt  | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) |
| Ru  | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.40 (3) | 0.00 (1) | 0.00 (1) | 0.00 (1) |
| Zn  | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (1) |

CO₂ binding over these models for academic interest and to compare them to other graphene systems.

**CO₂ bindings over M₂-SV, MPt-SV and M₂-TV models**

On the M₂-SV and MPt-SV models, CO₂ is often activated during adsorption. The adsorption free energies are mostly exergonic or close to thermoneutral over both models except for Mn-, Fe-, and Mo-based MPt-SV (more than 2.5 eV). We excluded the M₂-SV and MPt-SV electrodes from further studies as their formations are thermodynamically unstable and they have not been experimentally observed.

Among the M₂-TV electrodes, only Zn, Cu, and Al derivatives spontaneously bind and activate CO₂. The charge transfer by Al₂-TV electrode to the CO₂ molecule is reported as ∼0.3e, whereas, over Cu and Zn electrodes, rather high charge transfer (∼ -0.8 e) is
Figure S4: Sample optimized geometries of $M_2$TV: (a) both dopants above the graphene plane (b) one atom above and one below the graphene plane, and (c) the relative instabilities of former.

Table S2: Formation energy (eV) of graphene based electrodes.

| M    | M\_SV | M\_3N | M\_DV | M\_2SV | M\_4N | M\_2TV | M\_3SV | MPt\_SV |
|------|-------|-------|-------|--------|-------|--------|--------|---------|
| Ag   | 0.48  | -2.68 | -2.54 | -3.58  | -2.72 | 0.01   | 1.41   | 0.27    |
| Al   | -1.66 | -3.25 | -5.50 | -3.30  | -3.70 | -2.22  | -0.20  | 0.33    |
| Au   | 1.02  | -2.32 | -4.01 | 0.17   | -2.65 | -0.45  | 1.31   | 1.99    |
| B    | -7.63 | -4.11 | -6.45 | -6.67  | -3.49 | -4.61  | -1.68  | -1.72   |
| Co   | -1.49 | -2.60 | -3.89 | -1.66  | -3.36 | -1.18  | 0.56   | 0.73    |
| Cu   | 0.08  | -2.88 | -4.05 | -3.59  | -3.29 | -1.17  | 1.09   | 1.29    |
| Mn   | -3.09 | -3.17 | -5.62 | -3.34  | -3.79 | -2.58  | -0.99  | -0.53   |
| N    | -7.26 | -2.51 | -4.65 | -6.39  | -2.66 | -4.40  | -1.51  | -1.39   |
| Rh   | -1.63 | -2.26 | -3.70 | -1.89  | -3.17 | -1.03  | 1.13   | 0.79    |
| Cr   | -0.63 | -2.48 | -3.11 | -0.48  | -3.19 | 0.47   | 1.21   | 1.05    |
| Fe   | -1.50 | -2.87 | -4.04 | -1.97  | -3.43 | -1.71  | 0.31   | 0.29    |
| Mo   | 0.41  | -2.01 | -2.70 | -0.74  | -2.65 | 0.26   | 2.99   | 1.40    |
| Ni   | -0.82 | -2.78 | -3.76 | -1.38  | -3.47 | -1.57  | 0.82   | 0.55    |
| Pd   | -0.72 | -2.53 | -3.43 | -1.19  | -3.27 | -1.58  | 0.46   | 0.73    |
| Pt   | -1.01 | -2.19 | -4.79 | -1.59  | -3.34 | -1.97  | 0.54   | 0.54    |
| Ru   | -1.29 | -2.24 | -4.01 | -1.74  | -2.94 | -0.55  | 2.08   | 1.14    |
| Zn   | -0.36 | -3.12 | -3.69 | -2.75  | -3.52 | -1.24  | -0.13  | 0.95    |
Table S3: Formation energy (eV) corrected with zero-point energy (ZPE) of graphene based electrodes.

| M     | M_SV | M_3N | M_DV | M_2-2SV | M_4N | M_2-TV | M_3-SV | MPt_SV |
|-------|------|------|------|---------|------|--------|--------|--------|
| Ag    | 0.88 | -2.31| -1.94| -3.18   | -2.33| 0.36   | 1.61   | 0.48   |
| Al    | -1.25| -2.87| -4.92| -2.91   | -3.30| -1.84  | 0.02   | 0.56   |
| Au    | 1.40 | -1.94| -3.38| 0.50    | -2.27| -0.06  | 1.53   | 2.19   |
| B     | -7.03| -3.69| -5.74| -6.12   | -3.07| -4.10  | -1.35  | -1.41  |
| Co    | -1.07| -2.22| -3.28| -1.28   | -2.96| -0.79  | 0.80   | 0.96   |
| Cu    | 0.48 | -2.51| -3.42| -3.17   | -2.89| -0.81  | 1.29   | 1.50   |
| Mn    | -2.67| -2.78| -5.03| -2.95   | -3.40| -2.19  | -0.77  | -0.30  |
| N     | -6.67| -2.10| -3.90| -5.82   | -2.26| -3.85  | -1.13  | -1.06  |
| Rh    | -1.20| -1.89| -3.09| -1.52   | -2.77| -0.66  | 1.36   | 1.01   |
| Cr    | -0.22| -2.11| -2.51| -0.09   | -2.79| 0.87   | 1.43   | 1.28   |
| Fe    | -1.06| -2.50| -3.42| -1.59   | -3.03| -1.32  | 0.54   | 0.53   |
| Mo    | 0.82 | -1.65| -2.11| -0.36   | -2.26| 0.63   | 3.20   | 1.62   |
| Ni    | -0.40| -2.41| -3.13| -1.01   | -3.06| -1.18  | 1.05   | 0.79   |
| Pd    | -0.30| -2.16| -2.85| -0.86   | -2.87| -1.21  | 0.68   | 0.96   |
| Pt    | -0.60| -1.82| -4.19| -1.24   | -2.94| -1.59  | 0.78   | 0.78   |
| Ru    | -0.85| -1.88| -3.37| -1.36   | -2.54| -0.17  | 2.31   | 1.38   |
| Zn    | 0.05 | -2.74| -3.15| -2.39   | -3.13| -0.91  | 0.09   | 1.17   |

Table S4: Formation enthalpy (eV) of graphene based electrodes.

| M     | M_SV | M_3N | M_DV | M_2-2SV | M_4N | M_2-TV | M_3-SV | MPt_SV |
|-------|------|------|------|---------|------|--------|--------|--------|
| Ag    | 0.81 | -2.35| -2.02| -3.19   | -2.37| 0.35   | 1.58   | 0.44   |
| Al    | -1.35| -2.92| -4.99| -2.94   | -3.34| -1.87  | -0.04  | 0.50   |
| Au    | 1.34 | -1.99| -3.47| 0.48    | -2.31| -0.09  | 1.49   | 2.15   |
| B     | -7.16| -3.75| -5.83| -6.19   | -3.12| -4.16  | -1.43  | -1.48  |
| Co    | -1.17| -2.27| -3.36| -1.32   | -3.00| -0.83  | 0.74   | 0.91   |
| Cu    | 0.40 | -2.55| -3.51| -3.19   | -2.94| -0.83  | 1.25   | 1.46   |
| Mn    | -2.76| -2.84| -5.11| -2.98   | -3.45| -2.22  | -0.82  | -0.35  |
| N     | -6.79| -2.16| -4.00| -5.89   | -2.31| -3.91  | -1.22  | -1.14  |
| Rh    | -1.29| -1.94| -3.16| -1.55   | -2.82| -0.69  | 1.30   | 0.96   |
| Cr    | -0.32| -2.16| -2.57| -0.13   | -2.84| 0.83   | 1.38   | 1.23   |
| Fe    | -1.16| -2.55| -3.49| -1.62   | -3.07| -1.35  | 0.47   | 0.47   |
| Mo    | 0.73 | -1.70| -2.17| -0.39   | -2.30| 0.60   | 3.14   | 1.57   |
| Ni    | -0.49| -2.45| -3.22| -1.04   | -3.11| -1.21  | 1.00   | 0.73   |
| Pd    | -0.39| -2.20| -2.92| -0.88   | -2.92| -1.24  | 0.63   | 0.91   |
| Pt    | -0.68| -1.86| -4.27| -1.26   | -2.98| -1.62  | 0.73   | 0.73   |
| Ru    | -0.95| -1.93| -3.45| -1.40   | -2.59| -0.20  | 2.25   | 1.32   |
| Zn    | -0.03| -2.79| -3.21| -2.41   | -3.17| -0.93  | 0.04   | 1.13   |
### Table S5: Formation free energy (eV) of graphene based electrodes.

| M  | M_SV | M_3N | M_DV | M_2.2SV | M_4N | M_2.TV | M_2.SV | MPt_SV |
|----|------|------|------|---------|------|--------|--------|--------|
| Ag | 1.41 | -1.89| -1.43| -2.78   | -1.94| 0.79   | 2.05   | 0.95   |
| Al | -0.66| -2.45| -4.42| -2.50   | -2.89| -1.42  | 0.49   | 1.05   |
| Au | 1.94 | -1.53| -2.83| 0.98    | -1.86| 0.38   | 2.00   | 2.69   |
| B  | -6.47| -3.28| -5.28| -5.70   | -2.68| -3.69  | -0.87  | -0.94  |
| Co | -0.46| -1.79| -2.73| -0.81   | -2.55| -0.33  | 1.30   | 1.47   |
| Cu | 1.02 | -2.09| -2.88| 2.63   | -2.99| -1.72  | -0.29  | 0.20   |
| Mn | -2.08| -2.35| -4.47| -2.46   | -2.99| -1.72  | -0.29  | 0.20   |
| N  | -6.09| -1.68| -3.39| -5.37   | -1.87| -3.45  | -0.63  | -0.55  |
| Rh | -0.57| -1.47| -2.53| -1.03   | -2.36| -0.18  | 1.85   | 1.98   |
| Cr | 0.39 | -1.79| -2.79| -0.86   | -2.12| 0.31   | 2.85   | 1.90   |
| Fe | 1.44 | -1.32| -1.53| 0.15    | -1.84| 1.13   | 3.72   | 2.13   |
| Mo | 0.20 | -2.00| -2.58| -0.55   | -2.65| -0.73  | 1.55   | 1.30   |
| Ni | 0.30 | -1.75| -2.30| -0.42   | -2.46| -0.77  | 1.16   | 1.46   |
| Pt | 0.04 | -1.40| -3.50| -0.76   | -2.52| -1.10  | 1.31   | 1.31   |
| Ru | -0.19| -1.45| -2.79| -0.86   | -2.12| 0.31   | 2.85   | 1.90   |
| Zn | 0.60 | -2.33| -2.70| -1.97   | -2.74| -0.50  | 0.52   | 1.65   |

### Table S6: Magnetic moment (eV) and stable spin multiplicity (in the parenthesis) of CO₂ binding modified-graphene geometries.

| M  | M_SV | M_3N | M_DV | M_2.2SV | M_4N | M_2.TV | M_2.SV | MPt_SV |
|----|------|------|------|---------|------|--------|--------|--------|
| Ag | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Al | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Au | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| B  | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Co | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.09 (3) | 0.00 (2) |
| Cu | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Mn | 0.00 (2) | 0.04 (5) | 0.41 (4) | 0.86 (5) | 0.13 (4) | 2.83 (7) | 2.06 (7) | 0.16 (4) |
| N  | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Rh | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Cr | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Fe | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Mo | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Ni | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Pd | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Pt | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Ru | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
| Zn | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (2) | 0.00 (1) | 0.00 (1) | 0.00 (2) |
observed. Other $M_2$ TV electrodes are either unable to bind or activate CO$_2$.

![Figure S5: The optimized binding geometries of CO$_2$ over: a) Mn$_2$ SV, b) BPt SV, and c) Al$_2$ TV. The elements carbon, oxygen, and nitrogen are in grey, red, and blue colors, respectively.](image)
Table S7: Adsorption energy (eV) of CO$_2$ over heteroatom modified graphene based electrodes.

| M     | M_SV | M_3N | M_DV | M$_2$2SV | M_4N | M$_2$TV | M$_2$SV | MPt_SV |
|-------|------|------|------|----------|------|---------|--------|--------|
| Ag    | -0.34| -0.26| -0.20| -0.36    | -0.19| -0.39   | -0.36  | -0.29  |
| Al    | -0.31| -0.73| -0.28| -0.85    | 0.18 | -1.06   | -0.30  | -0.90  |
| Au    | 0.56 | -0.25| -0.21| -6.94    | -0.19| 0.00    | -0.32  | -0.54  |
| B     | -0.22| 0.47 | -0.44| -1.04    | 0.50 | -0.24   | -1.06  | -0.70  |
| Co    | -0.32| -1.08| -0.19| -0.74    | -0.24| 0.64    | -0.64  | -1.00  |
| Cu    | 0.18 | -0.31| -0.18| -0.55    | -0.17| -0.92   | -0.57  | -1.10  |
| Mn    | -0.13| -0.25| -0.23| -0.77    | 0.50 | -0.15   | -1.27  | 3.43   |
| N     | -0.20| -0.47| -0.23| -0.85    | -0.37| 0.51    | -0.33  | -0.63  |
| Rh    | -0.28| -1.12| -0.20| -0.36    | -0.23| 0.63    | -1.19  | -0.63  |
| Cr    | -0.67| -0.93| 0.97 | -1.94    | 0.02 | -0.25   | -1.54  | -1.49  |
| Fe    | -0.50| -0.95| -0.50| -0.54    | 0.35 | 1.33    | -0.73  | 2.08   |
| Mo    | -0.22| -1.23| -0.14| -1.18    | -1.42| -0.32   | -1.30  | 2.67   |
| Ni    | -0.33| -0.89| -0.18| -3.15    | -0.18| -0.48   | -1.06  | -0.55  |
| Pd    | -0.30| -0.39| -0.19| -0.32    | -0.21| -0.42   | -0.41  | -0.57  |
| Pt    | -0.27| -1.26| -0.21| -0.22    | -0.26| -0.46   | -0.50  | -0.50  |
| Ru    | -0.36| -0.85| -0.26| -0.53    | -0.41| 0.35    | -1.63  | -1.18  |
| Zn    | -0.47| -0.07| -0.23| -3.14    | -0.22| -1.99   | -0.33  | -1.03  |
Table S8: Adsorption energy (eV) corrected with zero-point energy (ZPE) of CO\textsubscript{2} over heteroatom modified graphene based electrodes.

| M     | M\textsubscript{SV} | 3N | D\textsubscript{V} | 2\textsubscript{SV} | 4N | T\textsubscript{V} | 2\textsubscript{SV} | MPt\textsubscript{SV} |
|-------|----------------------|----|---------------------|---------------------|----|---------------------|---------------------|---------------------|
| Ag    | -0.32                | -0.24 | -0.18               | -0.32               | -0.18 | -0.38               | -0.33               | -0.25               |
| Al    | -0.28                | -0.68 | -0.24               | -0.80               | 0.22  | -1.04               | -0.27               | -0.89               |
| Au    | 0.55                 | -0.21 | -0.18               | -6.75               | -0.16 | 0.01                | -0.29               | -0.52               |
| B     | -0.20                | 0.56  | -0.44               | -1.02               | 0.52  | -0.23               | -1.00               | -0.69               |
| Co    | -0.28                | -1.00 | -0.17               | -0.66               | -0.23 | 0.72                | -0.58               | -0.94               |
| Cu    | 0.17                 | -0.29 | -0.17               | -0.56               | -0.15 | -0.81               | -0.53               | -1.06               |
| Mn    | -0.11                | -0.18 | -0.21               | -0.70               | 0.55  | -0.04               | -1.25               | 3.43                |
| N     | -0.17                | -0.37 | -0.22               | -0.82               | -0.34 | 0.53                | -0.30               | -0.63               |
| Rh    | -0.26                | -1.04 | -0.18               | -0.31               | -0.22 | 0.69                | -1.15               | -0.60               |
| Cr    | -0.64                | -0.87 | 1.01                | -1.90               | 0.11  | -0.25               | -1.49               | -1.44               |
| Fe    | -0.51                | -0.84 | -0.49               | -0.46               | 0.43  | 1.34                | -0.66               | 2.12                |
| Mo    | -0.17                | -1.17 | -0.09               | -1.16               | -1.34 | -0.29               | -1.22               | 2.71                |
| Ni    | -0.29                | -0.82 | -0.17               | -3.04               | -0.16 | -0.44               | -1.02               | -0.53               |
| Pd    | -0.30                | -0.35 | -0.17               | -0.29               | -0.16 | -0.39               | -0.38               | -0.56               |
| Pt    | -0.24                | -1.20 | -0.17               | -0.17               | -0.24 | -0.43               | -0.48               | -0.48               |
| Ru    | -0.33                | -0.73 | -0.23               | -0.46               | -0.34 | 0.39                | -1.55               | -1.12               |
| Zn    | -0.44                | -0.08 | -0.20               | -3.02               | -0.20 | -1.90               | -0.31               | -1.00               |

Table S9: Adsorption enthalpy (eV) of CO\textsubscript{2} over heteroatom modified graphene based electrodes.

| M     | M\textsubscript{SV} | 3N | D\textsubscript{V} | 2\textsubscript{SV} | 4N | T\textsubscript{V} | 2\textsubscript{SV} | MPt\textsubscript{SV} |
|-------|----------------------|----|---------------------|---------------------|----|---------------------|---------------------|---------------------|
| Ag    | -0.30                | -0.22 | -0.16               | -0.32               | -0.15 | -0.36               | -0.31               | -0.24               |
| Al    | -0.27                | -0.69 | -0.23               | -0.83               | 0.23  | -1.06               | -0.26               | -0.89               |
| Au    | 0.58                 | -0.22 | -0.16               | -6.73               | -0.14 | 0.04                | -0.27               | -0.52               |
| B     | -0.18                | 0.54  | -0.45               | -1.00               | 0.52  | -0.20               | -1.00               | -0.69               |
| Co    | -0.27                | -1.01 | -0.15               | -0.69               | -0.21 | 0.69                | -0.60               | -0.96               |
| Cu    | 0.19                 | -0.27 | -0.14               | -0.56               | -0.15 | -0.85               | -0.51               | -1.07               |
| Mn    | -0.11                | -0.19 | -0.18               | -0.73               | 0.56  | -0.06               | -1.26               | 3.43                |
| N     | -0.15                | -0.39 | -0.19               | -0.80               | -0.32 | 0.55                | -0.28               | -0.61               |
| Rh    | -0.24                | -1.06 | -0.16               | -0.33               | -0.20 | 0.67                | -1.16               | -0.63               |
| Cr    | -0.65                | -0.87 | 1.00                | -1.92               | 0.09  | -0.26               | -1.51               | -1.45               |
| Fe    | -0.50                | -0.86 | -0.49               | -0.48               | 0.41  | 1.32                | -0.67               | 2.10                |
| Mo    | -0.18                | -1.17 | -0.10               | -1.17               | -1.35 | -0.29               | -1.24               | 2.70                |
| Ni    | -0.28                | -0.84 | -0.17               | -3.05               | -0.14 | -0.43               | -1.03               | -0.53               |
| Pd    | -0.27                | -0.35 | -0.15               | -0.28               | -0.13 | -0.38               | -0.39               | -0.56               |
| Pt    | -0.22                | -1.22 | -0.16               | -0.18               | -0.22 | -0.42               | -0.48               | -0.48               |
| Ru    | -0.32                | -0.73 | -0.21               | -0.48               | -0.35 | 0.37                | -1.57               | -1.14               |
| Zn    | -0.43                | -0.06 | -0.18               | -3.04               | -0.18 | -1.92               | -0.29               | -1.01               |
Figure S6: The flow-chart of a four-level selection criteria to study the electrocatalytic CO$_2$RR study.
Figure S7: The parametric details, namely, adsorption free energies of CO$_2$ ($G_\text{Ads}$), net charge transfer (q), and O–C–O angle, for the selection criteria over the considered electrodes: a) M$_\text{SV}$, b) M$_\text{3N}$, c) M$_\text{DV}$, d) M$_\text{2SV}$, e) M$_\text{4N}$, and f) M$_\text{2TV}$. The M$_\text{2SV}$ and MPt$_\text{SV}$ electrodes are omitted from electrocatalytic CO$_2$RR thermodynamics because of their high instabilities.
Figure S8: Linear scaling relationships between the binding free energies of COOH vs. CO$_2$ and COOH vs. CO over M$_3$N electrodes.
Figure S9: Linear scaling relationships between the binding free energies of COOH vs. CO\(_2\) and COOH vs. CO over M\(_2\)-2SV electrodes.
Table S10: Adsorption free energy (eV) of CO₂ over heteroatom modified graphene based electrodes.

| M   | M_SV | M_3N | M_DV | M_2-2SV | M_4N | M_2-TV | M_2-SV | MPt_SV |
|-----|------|------|------|---------|------|--------|--------|--------|
| Ag  | 0.06 | 0.10 | 0.15 | -0.03   | 0.14 | 0.01   | 0.04   | 0.13   |
| Al  | 0.06 | -0.24| 0.13 | -0.30   | 0.62 | -0.55  | 0.07   | -0.45  |
| Au  | 0.96 | 0.24 | 0.13 | -6.50   | 0.18 | 0.35   | 0.09   | -0.12  |
| B   | 0.11 | 1.01 | 0.02 | -0.68   | 0.97 | 0.11   | -0.59  | -0.30  |
| Co  | 0.11 | -0.54| 0.16 | -0.18   | 0.10 | 1.22   | -0.09  | -0.51  |
| Cu  | 0.56 | 0.06 | 0.14 | -0.09   | 0.23 | -0.27  | -0.17  | -0.65  |
| Mn  | 0.33 | 0.26 | 0.12 | -0.21   | 0.96 | 0.45   | -0.77  | 3.89   |
| N   | 0.13 | 0.09 | 0.11 | -0.49   | 0.06 | 0.92   | 0.06   | -0.25  |
| Rh  | 0.12 | -0.57| 0.16 | 0.15    | 0.09 | 1.17   | -0.72  | -0.14  |
| Cr  | -0.20| -0.46| 1.46 | -1.41   | 0.57 | 0.25   | -0.99  | -0.98  |
| Fe  | -0.12| -0.39| -0.10| 0.01    | 0.87 | 1.83   | -0.13  | 2.59   |
| Mo  | 0.31 | -0.74| 0.36 | -0.70   | -0.89| 0.15   | -0.68  | 3.18   |
| Ni  | 0.10 | -0.35| 0.16 | -2.62   | 0.17 | -0.02  | -0.59  | -0.12  |
| Pd  | 0.07 | 0.09 | 0.15 | 0.08    | 0.17 | 0.00   | 0.07   | -0.14  |
| Pt  | 0.13 | -0.73| 0.17 | 0.29    | 0.11 | -0.03  | -0.07  | -0.07  |
| Ru  | 0.03 | -0.28| 0.13 | 0.02    | 0.10 | 0.88   | -1.07  | -0.67  |
| Zn  | -0.05| 0.27 | 0.18 | -2.63   | 0.16 | -1.40  | 0.07   | -0.54  |
Table S11: The binding free energies (eV) of COOH and CO over considered electrodes.

| Electrode | M   | Al   | Co   | Cu   | Mn   | N    | Rh   | Cr   | Fe   | Mo   | Pd   | Pt   | Ru   | Zn   |
|-----------|-----|------|------|------|------|------|------|------|------|------|------|------|------|------|
| M.3N      | COOH| -0.30| —    | —    | —    | -0.52| -0.73| 0.47 | 0.16 | -0.31| 0.00 | -1.03| -0.49| —    |
|           | CO  | 0.21 | —    | —    | —    | -2.39| -1.62| -0.92| -1.39| -1.49| -1.14| -2.44| -1.73| —    |
| M.2-2SV   | COOH| —    | -0.07| —    | -0.55| 0.30 | —    | -0.71| —    | —    | —    | —    | -0.12| —    |
|           | CO  | —    | -0.34| —    | -0.71| —    | -0.53| —    | -0.70| —    | —    | —    | —    | -1.03|
| M.4N      | COOH| —    | —    | —    | —    | —    | —    | —    | —    | -0.43| —    | —    | -0.36| —    |
|           | CO  | —    | —    | —    | —    | —    | —    | —    | —    | —    | -1.31| —    | —    | -1.83|
| M.2-TV    | COOH| -0.27| —    | 0.97 | —    | —    | —    | —    | —    | —    | —    | —    | —    | 0.52 |
|           | CO  | -0.10| —    | 0.12 | —    | —    | —    | —    | —    | —    | —    | —    | —    | -0.86|
Figure S10: Electrochemical thermodynamics of CO$_2$ reduction reaction using PCET and ETPT mechanisms over graphene electrodes: a) N$_3$N, b) Rh$_3$N, c) Cr$_3$N, d) Fe$_3$N, e) Mo$_3$N, f) Pd$_3$N, g) Ru$_3$N, h) Co$_{2.2}$SV, i) Mn$_{2.2}$SV, j) Rh$_{2.2}$SV, k) Fe$_{2.2}$SV, l) Ru$_{4}$N, m) Al$_2$.TV, n) Cu$_2$.TV, and o) Zn$_2$.TV. The representation of x-axis is similar to as described in main manuscript.
Table S12: Calculated potentials (V) of electrocatalytic CO$_2$ reduction reaction to produce CO over selected electrodes using PCET and ETPT mechanisms.

| Electrode | Potential (V) | M   |
|-----------|---------------|-----|
|           | $U_{Eq}$      | Al  | Co  | Cu  | Mn  | N   | Rh  | Cr  | Fe  | Mo  | Pd  | Pt  | Ru  | Zn  |
| M_3N      | -1.22         | -   | -   | -   | 0.08| -0.31| -0.66| -0.42| -0.37| -0.54| 0.11| -0.25| -   |
|           | $U_L$ (ETPT)  | -1.91| -   | -   | -1.17| -0.91| -1.76| -1.38| -2.26| -0.73| -0.69| -0.86| -   |
|           | $U_L$ (PCET)  | -1.91| -   | -   | -0.31| -0.51| -1.30| -0.99| -0.52| -0.83| 0.00| -0.33| -   |
|           | $U_{OP}$ (ETPT)| 0.69| -   | -   | -   | 1.25| 0.61| 1.10| 0.96| 1.89| 0.19| 0.80| 0.61| -   |
|           | $U_{OP}$ (PCET)| 0.69| -   | -   | -   | 0.39| 0.21| 0.65| 0.57| 0.15| 0.29| 0.11| 0.08| -   |
|           | $U_{Eq}$      | -   | -0.94| -0.76| -0.85| -0.76| -   | -   | -   | -   | -0.60| -   | -   |
|           | $U_L$ (ETPT)  | -1.38| -   | -1.24| -1.18| -1.41| -   | -   | -   | -   | -0.81| -   | -   |
|           | $U_L$ (PCET)  | -1.13| -   | -1.24| -1.13| -1.41| -   | -   | -   | -   | -0.71| -   | -   |
|           | $U_{OP}$ (ETPT)| - | -0.43| -0.48| 0.33| 0.64| -   | -   | -   | -   | 0.21| -   | -   |
|           | $U_{OP}$ (PCET)| - | -0.19| -0.48| 0.28| 0.64| -   | -   | -   | -   | 0.10| -   | -   |
|           | $U_{Eq}$      | -   | -   | -   | -   | -   | -   | -   | -0.46| -   | -0.20| -   | -   |
| M_2_2SV   | $U_L$ (ETPT)  | -1.56| -   | -6.27| -   | -   | -   | -   | -   | -   | -0.47| -   | -   |
|           | $U_L$ (PCET)  | -1.56| -   | -1.80| -   | -   | -   | -   | -   | -2.96| -   | -0.48| -   |
|           | $U_{OP}$ (ETPT)| - | -   | -   | -   | -   | -   | -   | -2.96| 2.50| 0.28| -   | -   |
|           | $U_{OP}$ (PCET)| - | -   | -   | -   | 0.06| -   | -   | 0.27| -   | -   | -   | -   |
|           | $U_{Eq}$      | -1.06| -1.18| -   | -   | -   | -   | -   | -0.68| -   | -   | -   | -   |
| M_4N      | $U_L$ (ETPT)  | -1.56| -   | -6.27| -   | -   | -   | -   | -   | -   | -0.47| -   | -   |
|           | $U_L$ (PCET)  | -1.56| -   | -1.80| -   | -   | -   | -   | -   | -2.96| -   | -0.48| -   |
|           | $U_{OP}$ (ETPT)| 0.50| -5.10| -   | -   | -   | -   | -   | -0.52| 2.50| 0.28| -   | -   |
|           | $U_{OP}$ (PCET)| 0.50| -0.63| -   | -   | 0.06| -   | -   | 0.27| -   | -   | -   | -   |
| M_2_TV    | $U_L$ (ETPT)  | -1.56| -   | -8.45| -   | -   | -   | -   | -   | -   | -0.47| -   | -   |
|           | $U_L$ (PCET)  | -1.56| -   | -1.35| -   | -   | -   | -   | -   | -2.96| -   | -0.48| -   |
|           | $U_{OP}$ (ETPT)| 0.50| 7.76| -   | -   | -   | -   | -   | -0.52| 2.50| 0.28| -   | -   |
|           | $U_{OP}$ (PCET)| 0.50| 0.66| -   | -   | 0.06| -   | -   | 0.27| -   | -   | -   | -   |
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