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# Why heterogeneous single-atom catalysts preferentially produce CO in the electrochemical CO<sub>2</sub> reduction reaction†

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Formate and CO are competing products in the two-electron CO<sub>2</sub> reduction reaction (2e CO<sub>2</sub>RR), and they are produced via \*OCHO and \*COOH intermediates, respectively. However, the factors governing CO/formate selectivity remain elusive, especially for metal–carbon–nitrogen (M–N–C) single-atom catalysts (SACs), most of which produce CO as their main product. Herein, we show computationally that the selectivity of M–N–C SACs is intrinsically associated with the CO<sub>2</sub> adsorption mode by using bismuth (Bi) nanosheets and the Bi–N–C SAC as model catalysts. According to our results, the Bi–N–C SAC exhibits a strong thermodynamic preference toward \*OCHO, but under working potentials, CO<sub>2</sub> is preferentially chemisorbed first due to a charge accumulation effect, and subsequent protonation of chemisorbed CO<sub>2</sub> to \*COOH is kinetically much more favorable than formation of \*OCHO. Consequently, the Bi–N–C SAC preferentially produces CO rather than formate. In contrast, the physisorption preference of CO<sub>2</sub> on Bi nanosheets contributes to high formate selectivity. Remarkably, this CO<sub>2</sub> adsorption-based mechanism also applies to other typical M–N–C SACs. This work not only resolves a long-standing puzzle in M–N–C SACs, but also presents simple, solid criteria (*i.e.*, CO<sub>2</sub> adsorption modes) for indicating CO/formate selectivity, which help strategic development of high-performance CO<sub>2</sub>RR catalysts.

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## Introduction

Electroreduction of CO<sub>2</sub> to produce valuable chemicals *via* heterogeneous catalysis has emerged as an effective approach to alleviate the ongoing climate crisis caused by massive consumption of fossil fuels.<sup>1,2</sup> During a typical CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR), excess renewable electricity is utilized, and waste CO<sub>2</sub> is converted into C<sub>1</sub> products including CO, formate/HCOOH, CH<sub>4</sub>, CH<sub>3</sub>OH, and C<sub>2</sub>–C<sub>4</sub> products.<sup>3–5</sup> Generation of two-electron (2e) products, *i.e.*, CO and formate, is considered a worthwhile endeavour since it proceeds with low overpotentials (*e.g.*, 0.2–0.4 V) and high faradaic efficiencies (~99%). Moreover, for a given electrical energy input, generating such products is relatively more profitable than the generation of the aforementioned multi-electron products.<sup>6,7</sup> However, CO production and formate production are competitive, and there remains a scientific conundrum as to which factors determine the catalytic selectivity.<sup>8</sup>

The issue regarding selectivity is particularly noticeable for a novel class of heterogeneous catalysts, namely metal–carbon–nitrogen (M–N–C) single-atom catalysts (SACs), which are inexpensive and earth-abundant, and they exhibit great potential for facilitating the 2e CO<sub>2</sub>RR.<sup>9</sup> Intriguingly, almost all reported M–N–C SACs produce CO instead of formate as the major product in the 2e CO<sub>2</sub>RR.<sup>10–15</sup> An extreme example is bismuth (Bi), a well-established formate-producing catalyst;<sup>16–19</sup> however, when the Bi species is atomically dispersed, the as-prepared Bi–N–C SAC exhibits considerable selectivity toward CO formation.<sup>20</sup> Similarly, bulk indium (In) has a high formate selectivity up to 99%,<sup>21</sup> while the In–N–C SAC has been observed to produce CO predominantly.<sup>22</sup> The apparent ambiguity in CO/formate selectivity seriously hampers strategic optimization of catalytic performance, which calls for a better understanding of the underlying mechanism.

In this work, we address this ambiguity *via* first-principles computations with explicit consideration of electrode potentials and solvent effects. The CO-producing Bi–N–C SAC and formate-producing Bi nanosheets were chosen as model catalysts with which we can explore the factors that determine the CO<sub>2</sub>RR selectivity of M–N–C SACs. It is found that the CO<sub>2</sub> adsorption mode plays a key role in governing the CO/formate selectivity of the M–N–C catalysts. Under working potentials (*U*), CO<sub>2</sub> displays typical chemisorption behaviour on the Bi–N–C SAC but prefers physisorption on Bi nanosheets. Comprehensive structural and kinetic analyses indicate that

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protonation of the chemisorbed  $\text{CO}_2$  ( $^*\text{CO}_2$ ) preferentially generates the  $^*\text{COOH}$  intermediate instead of the  $^*\text{OCHO}$  intermediate, which makes the Bi-N-C SAC a CO-producing catalyst despite its higher thermodynamic affinity for  $^*\text{OCHO}$ \*. By contrast, the physisorption preference of  $\text{CO}_2$  on Bi nanosheets contributes to high formate selectivity. Particularly, this  $\text{CO}_2$  adsorption-based mechanism is also applicable for other active M-N-C SACs, which rationalizes existing experimental observations.

## Results and discussion

### Potential-dependent thermodynamics of the 2e $\text{CO}_2\text{RR}$ on the Bi-N-C SAC and Bi nanosheets

In recent years, a consensus has been achieved for the electrochemical 2e  $\text{CO}_2\text{RR}$ , which states that CO generation is associated with the  $^*\text{COOH}$  intermediate, and formate production involves the  $^*\text{OCHO}$  intermediate.<sup>23–27</sup> The thermodynamics of  $^*\text{COOH}$  and  $^*\text{OCHO}$  formation have been studied intensively with conventional first-principles modelling (*e.g.*, the constant-charge method), and they have been proposed as criteria to deduce the CO/formate selectivity. For example, it has been proposed that the high formate selectivity of Bi nanosheets can be attributed to their thermodynamic affinity for the key intermediate  $^*\text{OCHO}$  rather than  $^*\text{COOH}$ .<sup>28,29</sup> To this end, we first studied the thermodynamics for formation of  $^*\text{COOH}$  and  $^*\text{OCHO}$  on the Bi-N-C SAC, and Bi nanosheets with three-layer thickness were also studied for comparison (Fig. S1†). It is

found that  $^*\text{COOH}$  and  $^*\text{COHO}$  on the C and N sites of the Bi-N-C SAC spontaneously move to the Bi sites after structural optimization, and hence we focus on the Bi sites.

Considering that the accuracy of the conventional constant-charge method is undermined because it neglects the surface charge effect, we employed a constant-potential/hybrid-solvent approach to explore the thermodynamics of  $^*\text{COOH}$  and  $^*\text{OCHO}$  formation at a solid-liquid interface (see Methods for details). The optimized structures are shown in Fig. 1a and b, while the total energies of  $^*\text{OCHO}$  ( $E_{^*\text{OCHO}}$ ) and  $^*\text{COOH}$  ( $E_{^*\text{COOH}}$ ) as a function of working potential for the Bi-N-C SAC and Bi nanosheets are shown in Fig. 1c and d, respectively. Please note that the Bi-N-C SAC exhibited good stability during the  $\text{CO}_2\text{RR}$  as experimentally demonstrated.<sup>20</sup> To obtain theoretical insight into the stability, we computed the dissolution potential ( $U_{\text{dis}}$ ) of the Bi-N-C SAC, defined as  $U_{\text{dis}} = U_{\text{Bi}}^0 + (E_{\text{Bi,bulk}} - E_{\text{Bi,SAC}})/3e$ , where  $U_{\text{Bi}}^0$  is the standard dissolution potential,  $E_{\text{Bi,bulk}}$  is the energy of one Bi atom in the bulk, and  $E_{\text{Bi,SAC}}$  is the binding energy of one Bi atom in the Bi-N-C SAC. According to our calculations, the  $U_{\text{dis}}$  of the Bi-N-C SAC is as high as 0.33 V, suggesting that the Bi species is stable under working potentials. In addition, the structural integrity of the Bi-N-C SAC can be well maintained throughout a 10 ps first-principles molecular dynamics simulation at 300 K (Fig. S2†), indicating its high structural stability.

Notably, for both the Bi-N-C SAC and Bi nanosheets,  $E_{^*\text{OCHO}}$  is always lower than  $E_{^*\text{COOH}}$  under working potentials, indicating that the Bi species in these two catalysts have a higher

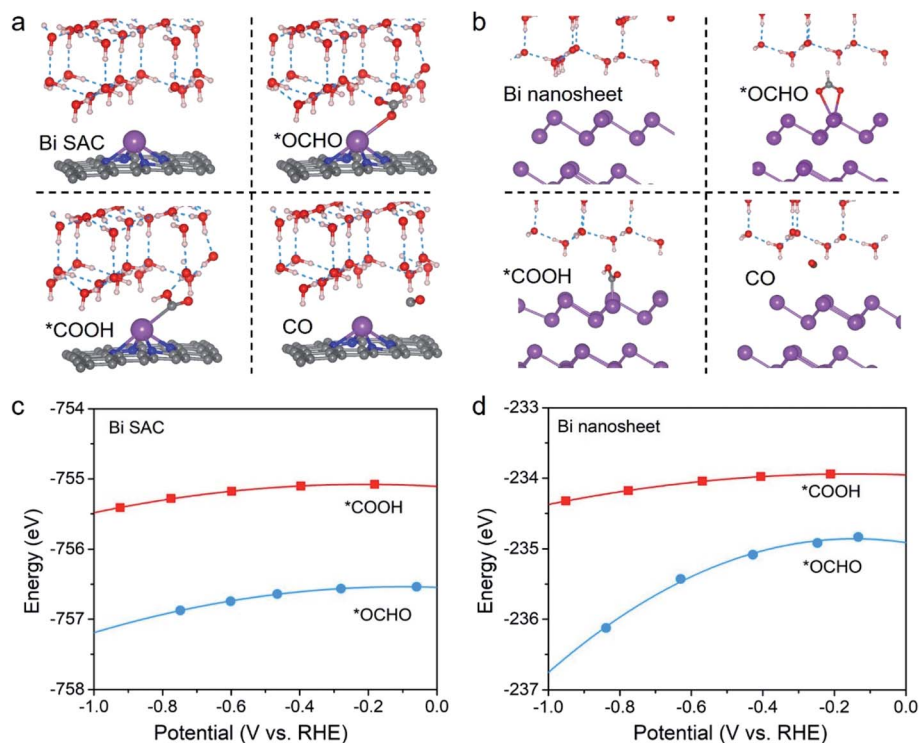


Fig. 1 Geometric structures of the 2e  $\text{CO}_2\text{RR}$  species for (a) the Bi-N-C SAC and (b) the Bi nanosheets. The violet, grey, red, and white spheres denote Bi, C, O, and H, respectively. The blue dashed lines indicate the hydrogen bond. Computed total energies of  $^*\text{OCHO}$  and  $^*\text{COOH}$  on (c) the Bi-N-C SAC and (d) the Bi nanosheets as a function of potential.

thermodynamic affinity toward  $^*\text{OCHO}$ . The results for Bi nanosheets were consistent with previous experimental measurements<sup>16–19,28</sup> and theoretical studies.<sup>28,29</sup> However, due to the higher thermodynamic affinity for  $^*\text{OCHO}$ , the Bi–N–C SAC is also thought to have formate selectivity, which contradicts the experimental result.<sup>20</sup> Actually, this does not mean that either the theoretical or the experimental results are wrong, since thermodynamic criteria for the selectivity of 2e  $\text{CO}_2\text{RR}$  often fail to give the rational indication. For example, silver (Ag)<sup>30</sup> and gold (Au)<sup>31</sup> are well-established CO-producing catalysts, but they both bind more strongly to  $^*\text{OCHO}$  than to  $^*\text{COOH}$ ,<sup>23</sup> analogous to the Bi–N–C SAC.

An important question then arises: why is a  $\text{CO}_2\text{RR}$  catalyst with higher thermodynamic affinity for  $^*\text{OCHO}$  not guaranteed to produce formate? To address this, we revisited previous thermodynamic computations and mechanistic schemes (Fig. S3†). A detailed examination of modelling results revealed that the thermodynamics of  $\text{CO}_2$  adsorption and the kinetics of  $\text{CO}_2$  protonation are usually overlooked or oversimplified.  $\text{CO}_2$  adsorption is crucial for the  $\text{CO}_2\text{RR}$  because  $\text{CO}_2$  molecules are activated with a net charge on the catalyst surface under a negative working potential. In most thermodynamic calculations, the effect of this net charge on the  $\text{CO}_2$  molecule is neglected, and instead an isolated, inactivated  $\text{CO}_2$  molecule is studied. Indeed, it has been demonstrated that formation of the chemisorbed  $\text{CO}_2$  molecule ( $^*\text{CO}_2$ ) plays a vital role in the  $\text{CO}_2\text{RR}$  for numerous catalysts.<sup>32–35</sup> Nevertheless, physisorbed  $\text{CO}_2$  may also contribute to the  $\text{CO}_2\text{RR}$ . For example, the one-step reduction process in which physisorbed  $\text{CO}_2$  reacts with surface-bound  $^*\text{H}$  has been established as the key pathway for formate production.<sup>36</sup>

### $\text{CO}_2$ adsorption mode of the Bi–N–C SAC and Bi nanosheets under working potentials

Based on the above analysis, we shifted our focus to  $\text{CO}_2$  adsorption on the Bi–N–C SAC and Bi nanosheets at working potentials. Remarkably, the adsorption configuration for  $\text{CO}_2$  was found to be significantly dependent on the working potential. This is evident in Fig. 2a; at  $U > -0.33$  V, the  $\text{CO}_2$  molecule maintains its original structure during physisorption on the Bi–N–C SAC, whereas chemisorption is energetically more favourable below a potential of  $-0.33$  V. Therefore,  $\text{CO}_2$  can be activated on the Bi–N–C SAC to form  $^*\text{CO}_2$  at the working potentials. The as-formed  $^*\text{CO}_2$  would lead to subsequent  $^*\text{COOH}$  formation rather than  $^*\text{OCHO}$  formation. This can be understood intuitively by inspecting the geometric structures of the two intermediates (Fig. S4†). The structures of  $^*\text{CO}_2$  and  $^*\text{COOH}$  share a similar configuration for the O–C–O moiety (exhibiting a V-shaped pattern), suggesting that a transition from the former to the latter is much more likely to occur than the  $^*\text{CO}_2$  to  $^*\text{OCHO}$  transformation, during which the O–C–O moiety must be inverted from a V-shaped pattern to a  $\Delta$ -shaped pattern. Please note that CO is physisorbed on the Bi–N–C SAC, and the chemisorbed CO state is unavailable at negative potentials (Fig. S5†), indicating that the generated CO species can be easily desorbed from the Bi–N–C SAC.

Compared with that on the Bi–N–C SAC, the  $\text{CO}_2$  molecule on Bi nanosheets adopts a physisorption configuration preferentially, as it is energetically more favourable than the chemisorption configuration over a wide range of potentials (Fig. 2b). It seems that  $\text{CO}_2$  could also be chemisorbed on Bi nanosheets when the potential is below  $-0.74$  V; however, at such potentials, the surface of the Bi nanosheets would be covered by  $^*\text{H}$



**Fig. 2** Calculated total energies of chemisorbed  $\text{CO}_2$  ( $^*\text{CO}_2$ ) and physisorbed  $\text{CO}_2$  of (a) the Bi–N–C SAC and (b) the Bi nanosheets as a function of potential  $U$ . Charge density difference for (c) the Bi–N–C SAC and (d) the Bi nanosheets when the applied potential changes from 0 to  $-0.6$  V. The iso-value is 0.0006 a.u.





instead of  $^*\text{CO}_2$ , and the production of formate proceeds through the surface hydrogenation mechanism.

Why is the adsorption behaviour of  $\text{CO}_2$  on the Bi–N–C SAC more sensitive to electrode potential than that on Bi nanosheets? In principle, a catalyst can gain net surface charge under negative working potential. For the Bi–N–C SAC, a considerable amount of additional charge is gained and largely located at the Bi site (Fig. 2c). For the Bi nanosheets, the amount of the additional charge is much smaller than that of the Bi–N–C SAC subjected to an equal potential change, and this charge is uniformly distributed on the Bi atoms at the surface (Fig. 2d). Therefore, the chemisorption preference for  $\text{CO}_2$  on the Bi–N–C SAC should be essentially attributed to the pronounced charge accumulation around the Bi site, which facilitates the adsorption and activation of  $\text{CO}_2$  to form  $^*\text{CO}_2$ .

### Potential-dependent kinetics analysis

To obtain more insight into the CO selectivity of the Bi–N–C SAC, we investigated the kinetics of  $^*\text{CO}_2$  protonation. Snapshots of the path for protonation of  $^*\text{CO}_2$  to  $^*\text{COOH}$  are shown in Fig. 3a. In accordance with our expectations, the kinetic barrier ( $\Delta G^\ddagger$ ) of  $^*\text{COOH}$  formation was found to be much smaller than that of  $^*\text{OCHO}$  formation under working potentials (Fig. 3b). For example, at  $U = -0.70$  V, the  $\Delta G^\ddagger$  of  $^*\text{COOH}$  formation is only 0.35 eV, which is much lower than that of  $^*\text{OCHO}$  formation (0.85 eV). As with many other electrochemical reactions,<sup>37,38</sup> the  $\Delta G^\ddagger$  of  $^*\text{COOH}$  formation also decreases with increasing negative potential, indicating that the

formation of  $^*\text{COOH}$  is kinetically more favourable at high working potentials.

Unexpectedly, the  $\Delta G^\ddagger$  of  $^*\text{CO}_2$ -to- $^*\text{OCHO}$  conversion on the Bi–N–C SAC increases as  $U$  increases. This is because to form  $^*\text{OCHO}$ , the chemisorbed  $\text{CO}_2$  (V-shaped pattern) should first desorb to adopt the physisorption configuration before bending to form an adsorbed O–C–O moiety with the  $\Lambda$ -shaped pattern (Fig. 3c), and specifically, the energy difference between the physisorbed  $\text{CO}_2$  configuration and chemisorbed  $\text{CO}_2$  configuration of the Bi–N–C SAC increases with the decrease of  $U$  (Fig. 3d). This situation implied that the chemisorbed  $\text{CO}_2$  configuration of the Bi–N–C SAC is more stable at lower potentials, and the structural conversion from the chemisorbed  $\text{CO}_2$  configuration to the physisorbed  $\text{CO}_2$  configuration is more energetically unfavourable, thereby leading to the increased  $\Delta G^\ddagger$  for  $^*\text{OCHO}$  formation at lower potentials.

The above results vividly indicate that although the formation of  $^*\text{OCHO}$  is thermodynamically favourable on the Bi–N–C SAC, it would be significantly suppressed by the formation of  $^*\text{COOH}$  due to kinetic factors. In contrast, for Bi nanosheets, the kinetic results based on the surface hydrogenation mechanism reveal that  $^*\text{OCHO}$  formation is kinetically more favourable than  $^*\text{COOH}$  formation (Fig. S6†), which is consistent with the thermodynamic data (Fig. 1d). For instance, at  $U = -0.74$  V,  $\Delta G^\ddagger$  of  $^*\text{OCHO}$  formation is 0.65 eV, which is much lower than that of  $^*\text{COOH}$  formation (0.94 eV). Overall, the above results demonstrate that the CO/formate selectivities of the Bi–N–C SAC and Bi nanosheets are intrinsically associated with the  $\text{CO}_2$  adsorption mode.



Fig. 3 Snapshots of the paths for the protonation of chemisorbed  $\text{CO}_2$  ( $^*\text{CO}_2$ ) to (a)  $^*\text{COOH}$  and (c)  $^*\text{OCHO}$  on the Bi–N–C SAC. (b) Kinetic barriers  $\Delta G^\ddagger$  for protonation of  $^*\text{CO}_2$  to form  $^*\text{COOH}$  and  $^*\text{OCHO}$  on the Bi–N–C SAC as a function of potential. The inset is the reaction path at  $U = -0.7$  V. (d) Energy difference between the physisorbed  $\text{CO}_2$  configuration and chemisorbed  $\text{CO}_2$  configuration ( $E_{\text{phy}} - E_{\text{chem}}$ ) of the Bi–N–C SAC as a function of potential. A more positive value of  $E_{\text{phy}} - E_{\text{chem}}$  indicates that the chemisorbed  $\text{CO}_2$  configuration is more stable.



## CO<sub>2</sub> adsorption mode serving as the criteria for indicating the 2e selectivity of other typical M–N–C SACs

Although only the Bi–N–C SAC was explicitly investigated in the present study, the CO<sub>2</sub> adsorption mode-based criteria are expected to be applicable to many other M–N–C SACs that show high CO selectivity. This is because that these M–N–C SACs should also exhibit charge accumulation effects under working potentials, which would promote CO<sub>2</sub> chemisorption and, from a kinetic perspective, protonation of \*CO<sub>2</sub> to give \*COOH. For this reason, we have evaluated the CO<sub>2</sub> adsorption performance of four M–N–C SACs (M = Fe, Co, Ni, and In), which are the most commonly studied SACs for the CO<sub>2</sub>RR in the literature.<sup>12–15,22</sup> As expected, the CO<sub>2</sub> molecule adopts a chemisorption configuration on all of these M–N–C SACs under working potentials (Fig. 4), which should contribute to high CO selectivity in the 2e CO<sub>2</sub>RR.

Further kinetic results also reveal that protonation of the chemisorbed CO<sub>2</sub> to \*COOH is kinetically much more favourable than that to \*OCHO, as shown in Fig. S7–S9,<sup>†</sup> where the Co–N–C SAC was explored as an example due to the high computational cost. Therefore, it is not surprising that almost all M–N–C SACs were observed to produce CO instead of formate as their main product in the 2e CO<sub>2</sub>RR. In contrast, the general criteria based on the thermodynamics of \*COOH/\*OCHO incorrectly indicate the selectivities of M–N–C SACs (M = Co, Ni, and In) (Fig. S10<sup>†</sup>).

To provide more insight into the CO<sub>2</sub> adsorption mode-based criteria, we also explored the CO<sub>2</sub> adsorption on the well-established Au and Ag catalysts of which the selectivity is incorrectly indicated by the thermodynamics of \*COOH/\*OCHO. As shown in Fig. S11,<sup>†</sup> Au and Ag preferentially adopt the CO<sub>2</sub> chemisorption configuration under typical working potentials, indicating that the CO<sub>2</sub> adsorption mode-based criteria also apply to Au and Ag.

## Conclusions

To summarize, a fundamental understanding of the high CO selectivity of heterogeneous M–N–C SACs has been provided in this work by means of constant-potential first-principles computations. It was found that under working potentials, the metal sites of M–N–C SACs are subjected to a charge accumulation effect, which would facilitate chemisorption of CO<sub>2</sub> molecules. Although the formation of \*OCHO is thermodynamically favoured, the chemisorbed \*CO<sub>2</sub> tends to be protonated to form \*COOH rather than \*OCHO due to the more favourable kinetics, and this ultimately leads to high CO selectivity. Our work provides new mechanical insights into the selectivity of the 2e CO<sub>2</sub>RR, which resolves a long-standing puzzle in M–N–C SACs. We expect our findings to provide useful guidance for improving the selectivity of M–N–C SACs as well as other catalysts for the CO<sub>2</sub>RR.

## Methods

### First-principles calculations

Spin-polarized first-principles calculations were performed using the projector-augmented wave approach,<sup>39</sup> as implemented in the Vienna *Ab initio* Simulation Package (VASP).<sup>40,41</sup> The electronic exchange–correlation energy was modelled using the BEEF-vdW functional,<sup>42</sup> which provides a good description of the intermediate adsorption. A *k*-space sampling of  $3 \times 3 \times 1$  and a cutoff energy of 400 eV were adopted in all calculations. The convergence thresholds for energy and atomic forces were set as  $5 \times 10^{-5}$  eV and 0.01 eV Å<sup>−1</sup>, respectively. For M–N–C SACs (M = Bi, Fe, Co, and In), a typical MN<sub>4</sub>-embedded graphene slab was constructed, which contains 44 carbon atoms, 4 pyridine-type nitrogen atoms, and 1 metal atom. There is still a debate about the active moiety of the Ni–N–C SAC, and herein a pyrrole-type NiN<sub>4</sub> moiety is adopted due to its favourable formation energy. For Bi nanosheets, according to previous studies,<sup>28,29</sup> a (2 × 2) Bi trilayer slab was modelled; the top two layers plus adsorbates are allowed to relax freely, while the bottom layer is fixed. For Au and Ag, the typical (111) slabs with a (2 × 2 × 4) supercell were constructed, where bottom two layers were frozen during structural optimization. The vacuum space of the slabs was set as ~30 Å to minimize interactions between periodic images. An explicit water bilayer was constructed to describe the solvation effect.

### Constant-potential computations

The Poisson–Boltzmann implicit solvation model was used to establish the relationship between charge (adding or removing extra electrons into the slab) and electrode potential (*U*).<sup>43,44</sup> This method takes advantage of that the electro-static potential goes to zero in the electrolyte region. For each reaction species, independent calculations with five different system charges were performed. For a charged slab, the potential with respect to the standard hydrogen electrode (SHE) was calculated by:

$$U_{\text{SHE}} = W_i/e - 4.6 \text{ V}$$

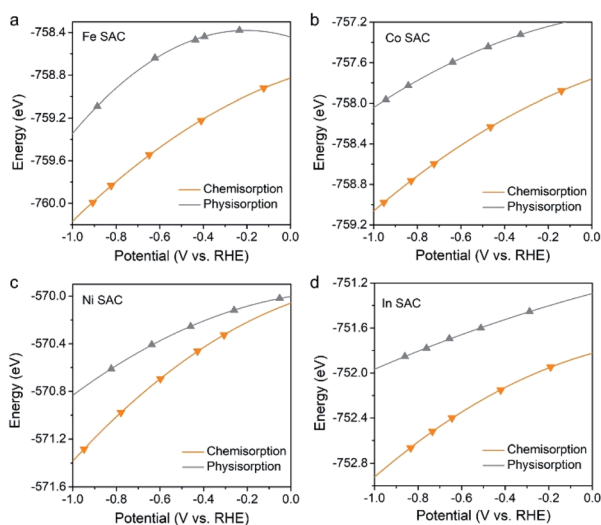


Fig. 4 Calculated total energies of chemisorbed and physisorbed CO<sub>2</sub> on the (a) Fe–N–C, (b) Co–N–C, (c) Ni–N–C, and (d) In–N–C SACs as a function of potential.



where  $W_f$  is the work function of the slab and the value of 4.6 represents the predicted standard hydrogen electrode scale.<sup>44</sup> The values of  $U_{\text{SHE}}$  were further regulated to the reversible hydrogen electrode (RHE) scale by a potential shift of  $0.0592 \times \text{pH}$ , where the value of pH was set as 7 in the work. Specifically, the total energy of the charged slab at the corresponding potential,  $E(U)$ , was calculated by including energy corrections for it is necessary to add or remove electrons and background charge on the electronic energy obtained from self-consistent calculations.<sup>45–49</sup> Then, for each species, we can deduce the energy at a given potential by fitting the five energy-potential points in a quadratic form.

Physisorbed and gas-phase  $\text{CO}_2$  (+0.33 eV) and  $\text{H}_2$  (+0.09 eV) have been corrected to account for the error in the description of the OCO backbone and  $\text{H}_2$  configuration.<sup>50</sup> The free energy of each species,  $G(U)$ , was determined by further considering the zero-point energy ( $E_{\text{ZPE}}$ ) and entropy ( $-TS$ ) contributions, which are derived from vibrational frequency analysis.

### Kinetics computations

The transition states were obtained by using the climbing-image nudged elastic band (CI-NEB) approach.<sup>51</sup> A set of CI-NEB calculations with different charges was performed to assess the potential-dependent barriers. All transition states were verified by vibrational frequency calculations (only one imaginary frequency).

### Data availability

The computational data supporting the findings can be found in the article and ESI† and are available from the authors upon reasonable request.

### Author contributions

Y. L. designed the research. W. Y. and T. L. performed all the computations. All authors analysed the data and wrote the paper.

### Conflicts of interest

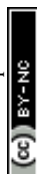
There are no conflicts to declare.

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