

## REVIEW

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## Recent advances in single atom catalysts for the electrochemical carbon dioxide reduction reaction

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The electrochemical carbon dioxide reduction reaction (CO<sub>2</sub>RR) offers a promising solution to mitigate carbon emission and at the same time generate valuable carbonaceous chemicals/fuels. Single atom catalysts (SACs) are encouraging to catalyze the electrochemical CO<sub>2</sub>RR due to the tunable electronic structure of the central metal atoms, which can regulate the adsorption energy of reactants and reaction intermediates. Moreover, SACs form a bridge between homogeneous and heterogeneous catalysts, providing an ideal platform to explore the reaction mechanism of electrochemical reactions. In this review, we first discuss the strategies for promoting the CO<sub>2</sub>RR performance, including suppression of the hydrogen evolution reaction (HER), generation of C<sub>1</sub> products and formation of C<sub>2+</sub> products. Then, we summarize the recent developments in regulating the structure of SACs toward the CO<sub>2</sub>RR based on the above aspects. Finally, several issues regarding the development of SACs for the CO<sub>2</sub>RR are raised and possible solutions are provided.

## 1. Introduction

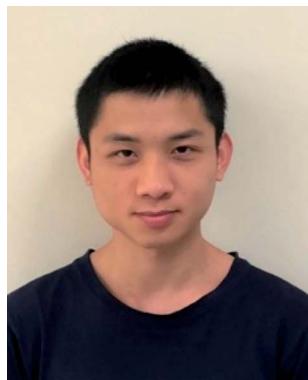
Excessive emission of CO<sub>2</sub> resulting from overconsumption of fossil fuels causes the green-house effect. The CO<sub>2</sub>RR not only provides a solution to reduce CO<sub>2</sub> concentration in the atmosphere, but also is able to simultaneously produce valuable carbonaceous chemicals/fuels.<sup>1,2</sup> Electrocatalytic reduction of CO<sub>2</sub> driven by renewable electricity is environmentally friendly, and has become a hotspot in the field of CO<sub>2</sub> conversion. The CO<sub>2</sub>RR involves very complex reactions, coupled with multiple

proton and electron transfer steps,<sup>3</sup> which can convert CO<sub>2</sub> into carbon monoxide (CO), methane (CH<sub>4</sub>), formic acid (HCOOH), methanol (CH<sub>3</sub>OH), ethylene (C<sub>2</sub>H<sub>4</sub>), ethanol (C<sub>2</sub>H<sub>5</sub>OH), etc:

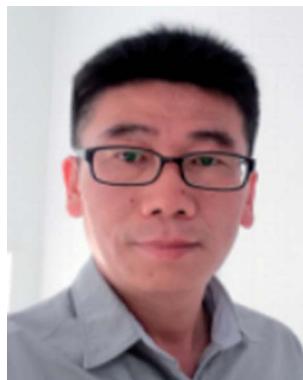


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| CO    | HCOOH |    |    | CH <sub>3</sub> OH |    |    | CH <sub>4</sub> |    |    | C <sub>2+</sub> |    |    |    |
|-------|-------|----|----|--------------------|----|----|-----------------|----|----|-----------------|----|----|----|
| Sc    | Ti    | V  | Cr | Mn                 | Fe | Co | Ni              | Cu | Zn | Ga              | Ge | As | Se |
| Y     | Zr    | Nb | Mo | Tc                 | Ru | Rh | Pd              | Ag | Cd | In              | Sn | Sb | Te |
| La-Lu | Hf    | Ta | W  | Re                 | Os | Ir | Pt              | Au | Hg | Tl              | Pb | Bi | Po |

Fig. 1 The reported elements in SACs for the electrochemical CO<sub>2</sub>RR.

Many catalysts have been explored to break the robust C=O bond, such as sulfides,<sup>4–6</sup> phosphides,<sup>7,8</sup> oxides,<sup>9–13</sup> and so on. However, the performance of the CO<sub>2</sub>RR is still unsatisfactory, showing low activity and poor product selectivity,<sup>14,15</sup> especially for liquid C<sub>2+</sub> products. Therefore, developing highly active catalysts with good selectivity and stability is crucial for promoting this clean energy conversion technology.<sup>16–18</sup>

Since Qiao *et al.*<sup>19</sup> developed the Pt<sub>1</sub>/FeO<sub>x</sub> single atom catalyst (SAC) in 2011, SACs have received considerable attention. SACs usually consist of a metal center coordinated with non-metal atoms. Because most of the metal sites can be exposed at the catalyst's surface and they possess a unique electronic structure, SACs show high intrinsic catalytic activity.<sup>20–23</sup> Additionally, SACs are ideal models for elucidating the structure–activity relationship because of their homogeneous atomically-dispersed active sites.<sup>24–27</sup> Furthermore, coupled with *in situ* characterization techniques, the structural evolution of active sites in SACs can be probed, which helps to further design next-generation catalysts.<sup>28,29</sup> Recently, the application of SACs achieved significant advancement in the field of electrochemical reactions.<sup>7,30</sup> In the electrochemical CO<sub>2</sub>RR, SACs exhibit encouraging performance in terms of catalytic activity, product selectivity, and stability.<sup>31–33</sup> Fig. 1 summarizes the reported elements in SACs for the electrochemical CO<sub>2</sub>RR.

The metal elements used to construct SACs for the electrochemical CO<sub>2</sub>RR include three types, transition metal (Mo, Fe, Co, Ni, Cu, and Zn), noble metal (Pd, Ag and Ir) and p-block (Sn, Sb and Bi) elements (Fig. 1). Most of the reported SACs electrochemically reduce CO<sub>2</sub> to CO, especially TM-SACs. However,

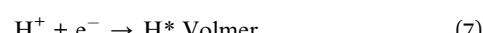
it is also reported that Co, Cu, Mo, Sn and Sb SACs can reduce CO<sub>2</sub> to liquid products (*e.g.*, HCOOH, CH<sub>3</sub>OH, *etc.*). As shown in Fig. 1, for the same metal SAC, the reported major CO<sub>2</sub>RR products are different, for example, Co-SAC can reduce CO<sub>2</sub> to CO or CH<sub>3</sub>OH, and Sn and Sb-SAC can reduce CO<sub>2</sub> to CO or HCOOH. The determining factor for product selectivity is still under controversy. Therefore, to clearly elucidate the structure–activity relationship in the CO<sub>2</sub>RR and further develop SACs with higher product selectivity, especially for C<sub>2+</sub> products, a systematic review of previous studies of SACs in the CO<sub>2</sub>RR is urgently needed. Fig. 2 shows the development of SAC-based electrocatalysts for the CO<sub>2</sub>RR.

In this review, the strategies to enhance the CO<sub>2</sub>RR performance are first outlined, including the suppression of the HER, and the generation of C<sub>1</sub> products and C<sub>2+</sub> products. Then, recent advances in promoting CO<sub>2</sub>RR performance using SACs are summarized. Finally, some challenges in this field are proposed and possible solutions are provided at the end.

## 2. Strategies to improve the CO<sub>2</sub>RR

### 2.1. Suppression of the HER

The HER is the main side reaction competing with the CO<sub>2</sub>RR. The HER can proceed *via* two mechanisms, the Volmer–Heyrovsky and the Volmer–Tafel mechanism.<sup>34–36</sup> In the Volmer step, a proton from the electrolyte reacts with an electron to form an adsorbed hydrogen on the catalyst surface (H\*). If the second step is the Heyrovsky reaction, the H\* will directly react with a proton and another electron to generate H<sub>2</sub>. If the Tafel reaction happens, another proton combines with another electron to form a second H\*, which will couple with the first H\* to generate H<sub>2</sub>.

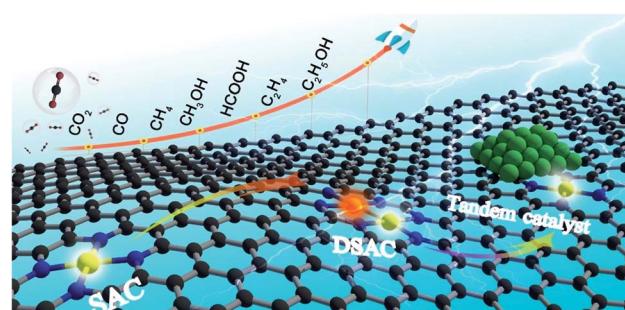


The Tafel route requires two adjacent active sites to adsorb two H\*, which is difficult in the case of SACs. So, the Heyrovsky mechanism is more plausible for the HER on SACs. Previous studies have shown that the activation energy of the Heyrovsky

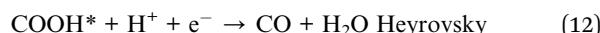


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Fig. 2 The development of SAC-based electrocatalysts for the CO<sub>2</sub>RR.

step is typically two times that of the Tafel step. Consequently, the HER can be considerably suppressed on SACs compared to their nanoparticle counterparts. A similar principle is also applicable to the  $\text{CO}_2$ RR, where the Heyrovsky mechanism is more plausible.



The difference between the thermodynamic limiting potentials ( $U_L(\text{CO}_2) - U_L(\text{H}_2)$ ) is a descriptor to indicate the selectivity of the  $\text{CO}_2$ RR ( $U_L(\text{CO}_2)$  and  $U_L(\text{H}_2)$  are the thermodynamic limiting potentials for the  $\text{CO}_2$ RR and HER, respectively). The larger the value, the higher the selectivity of CO.

The HER is the main side reaction competing with the  $\text{CO}_2$ RR, which needs to be suppressed so as to improve the selectivity of the  $\text{CO}_2$ RR. Jung *et al.* calculated the adsorption

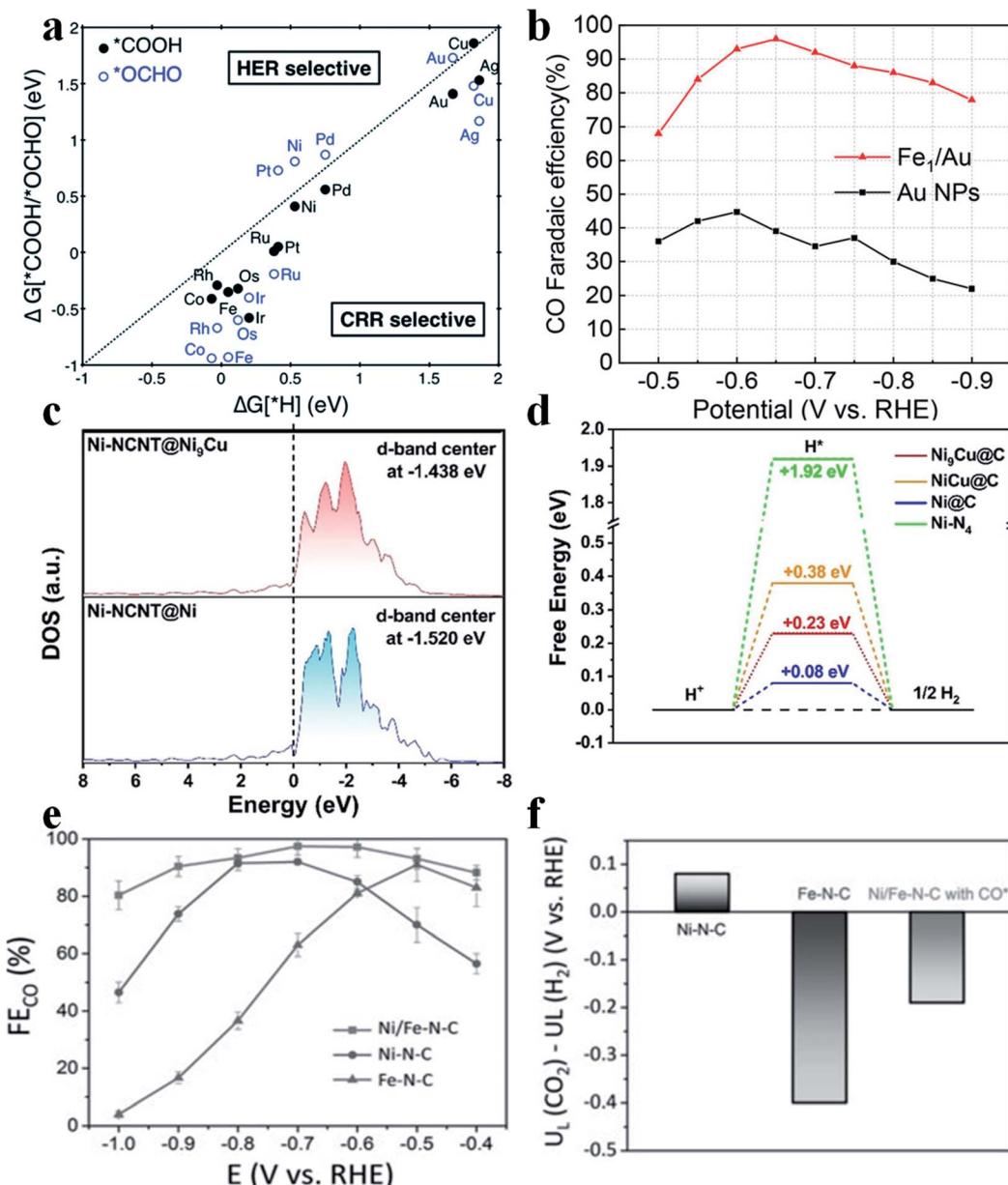


Fig. 3 (a) Free energy change of the first protonation step in the  $\text{CO}_2$ RR and HER on various SACs. Catalysts below the dotted parity line are  $\text{CO}_2$ RR selective. Reproduced with permission from ref. 7. Copyright (2017) The Royal Society of Chemistry. (b) CO faradaic efficiency of  $\text{Fe}_1/\text{Au}$ , compared with Au NPs, at different applied cathodic potentials. Reproduced with permission from ref. 37. Copyright (2020) American Chemical Society. (c) Calculated DOS for  $\text{Ni}^1\text{-NCNT@Ni}$  and  $\text{Ni}^1\text{-NCNT@Ni}_9\text{Cu}$ . (d) The calculated free-energy diagram of the HER on the (111) surface of  $\text{Ni@C}$ ,  $\text{Ni}_9\text{Cu@C}$ ,  $\text{NiCu@C}$ , and  $\text{Ni-N}_4$  sites. Reproduced with permission from ref. 38. Copyright (2020) Wiley-VCH. (e)  $\text{FE}_{\text{CO}}$  of  $\text{Ni/Fe-N-C}$ ,  $\text{Ni-N-C}$  and  $\text{Fe-N-C}$  at various applied potentials. (f) Difference in limiting potentials for the  $\text{CO}_2$ RR and HER for different catalysts. Reproduced with permission from ref. 39. Copyright (2019) Wiley-VCH.

energy of H ( $\Delta G(H^*)$ ),  $^*\text{COOH}$  and  $^*\text{OCHO}$  ( $\Delta G[^*\text{COOH}/^*\text{OCHO}]$ ) and found that most SACs possess a  $\Delta G(H^*)$  larger than the  $\Delta G[^*\text{COOH}/^*\text{OCHO}]$ , suggesting that the  $\text{CO}_2\text{RR}$  was more favorable than the HER on most SACs (Fig. 3a).<sup>7</sup> Although the HER is intrinsically unfavorable on SACs, the selectivity towards  $\text{CO}_2\text{RR}$  products still needs to be further improved. Yao *et al.* reported that by introducing Fe atoms into Au nanoparticles (Au NPs), the HER could be effectively suppressed, which greatly enhanced the CO faradaic efficiency (FE) in the  $\text{CO}_2\text{RR}$ .<sup>37</sup> Furthermore, the introduced Fe atoms bound with O atoms in  $\text{CO}_2$ , while the nearby Au atoms bound with C atoms in  $\text{CO}_2$ . Such a synergistic effect boosted the performance of Fe/Au (Fig. 3b). Other metal elements have also been studied to constrain the HER in SACs. Liu *et al.* introduced Cu into Ni SAC to form Ni(i)-NCNT@Ni<sub>9</sub>Cu to tune the adsorption energy of  $\text{H}^*$ . Electrochemical results showed that Ni(i)-NCNT@Ni<sub>9</sub>Cu delivered a specific current density of  $-32.87 \text{ mA cm}^{-2}$  and a TOF of  $1962 \text{ h}^{-1}$  at an overpotential of  $620 \text{ mV}$  for generating CO with 97%  $\text{FE}_{\text{CO}}$ . DFT calculations found that the d-band center was upshifted from  $-1.520 \text{ eV}$  to  $-1.438 \text{ eV}$  after the introduction of Cu, which strengthened the adsorption of  $\text{H}^*$  and thus further impeded the HER (Fig. 3c and d).<sup>38</sup> The HER dominates at high overpotentials in single Fe atom catalysts. Zhao *et al.* introduced single Ni atoms into Fe-SAC and found that such a dual atom center could efficiently regulate the adsorption energy of  $\text{H}^*$ <sup>39</sup> to suppress the HER and thus promote  $\text{FE}_{\text{CO}}$  (Fig. 3e and f).

Another issue in the electrochemical  $\text{CO}_2\text{RR}$  is that the solubility of  $\text{CO}_2$  in aqueous electrolyte is typically low (34 mM),<sup>40</sup> and the reactant diffusion limitation restricts the reaction rate of the  $\text{CO}_2\text{RR}$  particularly at high overpotentials, while the HER becomes more competitive. To tackle this challenge, many strategies have been developed, such as increasing the device pressure,<sup>41</sup> lowering the reaction temperature,<sup>42</sup> adopting a flow-cell device,<sup>43</sup> and using a solid electrolyte.<sup>44</sup>

## 2.2. Generation of $\text{C}_1$ products

$\text{C}_1$  products from the  $\text{CO}_2\text{RR}$  include CO,  $\text{HCOO}^-$ ,  $\text{CH}_3\text{OH}$ , and  $\text{CH}_4$ . Fig. 4 lists the possible pathways for the  $\text{C}_1$  products. To reduce  $\text{CO}_2$  to CO,  $^*\text{COOH}$  is first generated on the catalyst's surface *via* a proton coupled electron transfer (PCET) step, followed by  $^*\text{CO}$  formation through dehydrogenation of  $^*\text{COOH}$ , which is finally desorbed from the catalyst to release CO.<sup>45</sup> If the catalyst adsorbs  $^*\text{CO}$  very strongly, the catalytically active sites will be poisoned and the HER becomes dominant. If the catalyst adsorbs  $^*\text{CO}$  loosely,  $^*\text{CO}$  will be desorbed from the catalyst surface to generate CO. Only when the catalytic surface adsorbs  $^*\text{CO}$  neither too strongly nor too weakly, further reduction reaction can take place.  $\text{HCOO}^-$  is formed *via* the  $^*\text{OCHO}$  intermediate, which has a medium adsorption energy.<sup>46</sup>  $^*\text{OCHO}$  can be bound to the catalyst surface *via* one or two oxygen atoms. As there are no neighbouring active sites,  $^*\text{OCHO}$  is more likely to bind to the SAC *via* only one O atom as shown in Fig. 4. Both  $^*\text{CHO}$  and  $^*\text{COH}$  pathways are able to produce  $\text{CH}_4$ , forming  $^*\text{CHOH}$  and then  $^*\text{CH}_2\text{OH}$  and finally branching into two routes ( $\text{CH}_3\text{OH}$  and  $\text{CH}_4$ ).<sup>47–51</sup>  $^*\text{C}$  is formed *via* dehydration of  $^*\text{COH}$  and constitutes another pathway to generate  $\text{CH}_4$ . Carbon deposition covered on the copper catalyst after the  $\text{CO}_2\text{RR}$  confirmed the existence of  $^*\text{C}$ . Furthermore,  $^*\text{CH}_3\text{O}$  formed *via* protonation of  $^*\text{CHO}$  is an important intermediate for  $\text{CH}_4$  and  $\text{CH}_3\text{OH}$ .<sup>50,52–56</sup> It is worth mentioning that the energy barriers for both pathways ( $^*\text{CH}_2\text{OH}$  and  $^*\text{CH}_3\text{O}$ ) to produce  $\text{CH}_3\text{OH}$  are high, making  $\text{CH}_3\text{OH}$  generation rather difficult.

## 2.3. Generation of $\text{C}_2$ products

$\text{C}_2$  products from the  $\text{CO}_2\text{RR}$  include  $\text{C}_2\text{H}_4$ ,  $\text{C}_2\text{H}_5\text{OH}$ ,  $\text{C}_2\text{H}_6$ ,  $\text{CH}_3\text{COOH}$ ,  $\text{C}_2\text{H}_6\text{O}_2$ , *etc.* Several protonation and electron transfer steps engage in the formation of  $\text{C}_2$  products, making the reactions very sophisticated. As many possible pathways are capable of generating the same product, this leads to controversy about the reaction mechanisms.

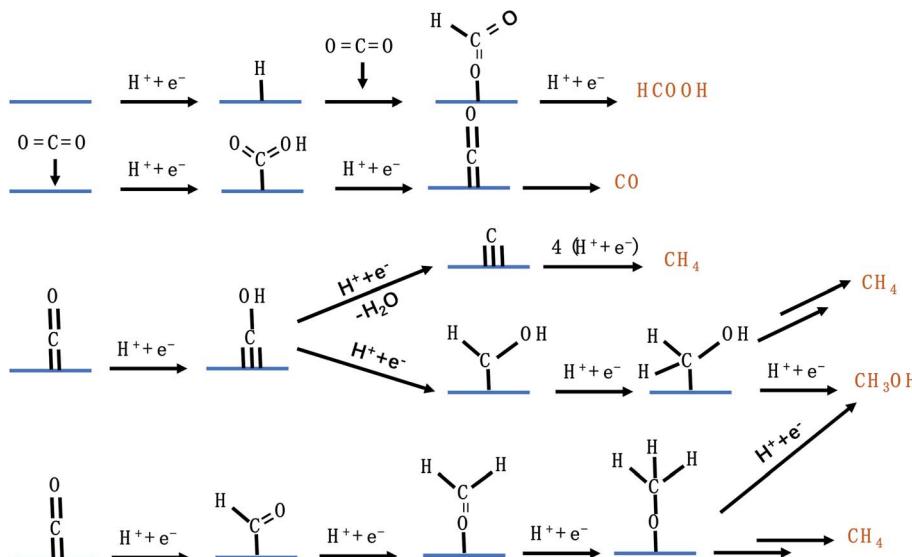


Fig. 4 The possible  $\text{CO}_2\text{RR}$  pathways for  $\text{C}_1$  products.



Fig. 5 shows the possible CO<sub>2</sub>RR pathways for C<sub>2</sub> products. In the first route, CH<sub>2</sub>CHO\* acts as an important intermediate to produce C<sub>2</sub>H<sub>4</sub> and CH<sub>3</sub>CH<sub>2</sub>OH,<sup>57</sup> which can branch into two pathways. One transforms to \*C<sub>2</sub>H<sub>4</sub>O, which dissociates and releases C<sub>2</sub>H<sub>4</sub>. The other forms CH<sub>3</sub>CHO\* which is further reduced to generate CH<sub>3</sub>CH<sub>2</sub>OH. It is noteworthy that the calculated energy barrier for CH<sub>3</sub>CHO\* → CH<sub>3</sub>CH<sub>2</sub>OH is 0.2 eV, which is higher than that for CH<sub>2</sub>CHO\* → \*O + C<sub>2</sub>H<sub>4</sub>, explaining the higher selectivity for C<sub>2</sub>H<sub>4</sub> than for CH<sub>3</sub>CH<sub>2</sub>OH among different C<sub>2</sub> products.<sup>58–62</sup> In the second route, starting from \*CO, CH<sub>2</sub>OHCH<sub>2</sub>OH can be formed through CO insertion into \*CHO coupled with several protonation and electron transfer steps. \*CHO can also undergo another pathway to produce CH<sub>4</sub>. The pathway towards CH<sub>4</sub> production has a lower energy barrier than that towards CH<sub>2</sub>OHCH<sub>2</sub>OH production, disclosing that very little CH<sub>2</sub>OHCH<sub>2</sub>OH can be detected. In the third route, \*CH<sub>2</sub>, originating from \*CO, serves as an important intermediate to produce CH<sub>3</sub>COOH and C<sub>2</sub>H<sub>6</sub>.<sup>63–66</sup> As discussed above, the C<sub>2</sub> pathways involve two close active sites to adsorb intermediates, which are severely limited in SACs. Consequently, very few groups have reported the generation of C<sub>2</sub> products on SACs *via* the CO<sub>2</sub>RR.

### 3. SACs for the CO<sub>2</sub>RR

#### 3.1. Advantages of SACs

Compared with traditional catalysts, the metal single atom sites in SACs locate at the catalyst's surface. Such an attribute makes SACs possess maximum atom utilization efficiency and thus exhibit excellent catalytic performance. Furthermore, the metal centers in SACs can be influenced by the near-range coordination environment and long-range interactions. Therefore, the electronic structure of SACs is tunable, which helps to improve the selectivity of the CO<sub>2</sub>RR. Also, SACs are ideal models for exploring the structure–activity relationship because of their homogeneous atomically-dispersed metal active centers.

#### 3.2. CO<sub>2</sub> to CO

Various strategies have been developed to promote the catalytic performance of SACs for the CO<sub>2</sub>RR to CO, including regulation of the center metal atom and manipulation of the coordination environment of the center metal atom. Recently, great achievements have been made in the production of CO from CO<sub>2</sub> on SACs. But, for commercial applications, further improvements in intrinsic catalytic activity and stability are needed. In this section, the developed strategies to promote the production of CO on SACs *via* the CO<sub>2</sub>RR are summarized.

##### 3.2.1. Modulation of the metal atomic center for boosting CO<sub>2</sub> reduction to CO.

SACs with different metal centers possess different d-band centers, which determine their catalytic performance in the CO<sub>2</sub>RR. Typically, the higher the d-band center is, the stronger the SAC binds with the intermediates. Jiang *et al.* synthesized various SACs implanted in N-doped carbon (M<sub>1</sub>-N-C; M = Fe, Co, Ni, and Cu) by calcining metal-organic frameworks (MOF).<sup>67</sup> Aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) images showed sparsely distributed bright dots, and Fourier transformed extended X-ray absorption fine structure (FT-EXAFS) spectra confirmed the absence of M–M bonds in all SACs, indicating that the metal atoms were atomically dispersed. In the N K-edge near-edge X-ray absorption fine structure (NEXAFS) spectra, a peak was found broadened and split into a doublet (a1 and a2), revealing that the metal atoms were stabilized by pyridinic N. EXAFS fitting results further showed that the metal centers in all SACs were coordinated with four pyridinic N atoms. Besides, all SACs possessed a similar N content and metal loading amount (about 4.94 at% and 1.75 wt%, respectively). Electrochemical results exhibited that Ni<sub>1</sub>-N-C had the best activity and selectivity towards CO production, followed by Fe<sub>1</sub>-N-C, Co<sub>1</sub>-N-C, and Cu<sub>1</sub>-N-C. Specifically, the TOF and CO partial current density of Ni<sub>1</sub>-N-C reached 11 315 h<sup>-1</sup> and 27 mA cm<sup>-2</sup>, respectively, at –0.8 V

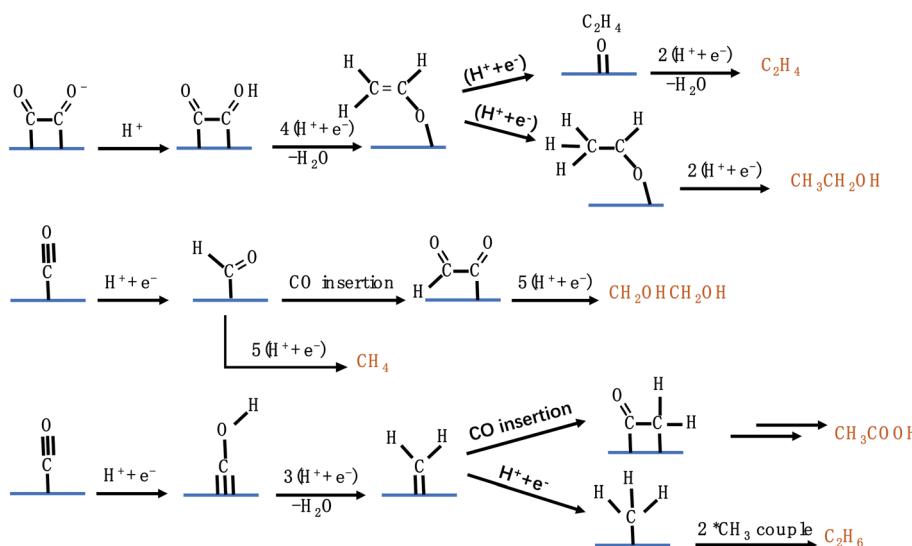


Fig. 5 The possible CO<sub>2</sub>RR pathways for C<sub>2</sub> products.



vs. RHE.  $\text{Ni}_{1\text{-N-C}}$  displayed a much smaller Tafel slope (98 mV per decade) than the other SACs (104 mV per decade for  $\text{Fe}_{1\text{-N-C}}$ , 142 mV per decade for  $\text{Co}_{1\text{-N-C}}$ , and 118 mV per decade for  $\text{Cu}_{1\text{-N-C}}$ ). Additionally,  $\text{Ni}_{1\text{-N-C}}$  also showed long-term durability at  $-0.8\text{ V}$  vs. RHE for 10 h without obvious attenuation in terms of current density and  $\text{FE}_{\text{CO}}$ . Density functional theory (DFT) calculations were performed to explain the differences among these SACs. As stated above, all SACs have similar structural parameters except for the metal centers, and offer an ideal model to study the role of metal atomic centers in  $\text{CO}_2\text{RR}$  performance. The calculated free energy diagram revealed that the formation of  $^{*}\text{COOH}$  was the rate-determining step (RDS) for all SACs.  $\text{Ni}_{1\text{-N-C}}$  and  $\text{Fe}_{1\text{-N-C}}$  had a similar energy barrier for  $^{*}\text{COOH}$  formation, lower than that of  $\text{Co}_{1\text{-N-C}}$  and  $\text{Cu}_{1\text{-N-C}}$ . Besides, the energy barrier for CO desorption on  $\text{Ni}_{1\text{-N-C}}$  was lower than that on  $\text{Fe}_{1\text{-N-C}}$ , suggesting favorable CO release from  $\text{Ni}_{1\text{-N-C}}$  (Fig. 6a). The  $U_{\text{L}}(\text{CO}_2) - U_{\text{L}}(\text{H}_2)$  values for  $\text{Ni}_{1\text{-N-C}}$ ,  $\text{Fe}_{1\text{-N-C}}$ ,  $\text{Co}_{1\text{-N-C}}$  and  $\text{Cu}_{1\text{-N-C}}$  are  $-1.19\text{ eV}$ ,  $-1.55\text{ eV}$ ,  $-1.98\text{ eV}$ , and  $-2.33\text{ eV}$ , respectively. The most positive value of  $U_{\text{L}}(\text{CO}_2) - U_{\text{L}}(\text{H}_2)$  for  $\text{Ni}_{1\text{-N-C}}$  supported the conclusion that  $\text{Ni}_{1\text{-N-C}}$  had the highest selectivity towards CO production (Fig. 6b). Peter *et al.* also prepared a series of transition metal SACs ( $\text{Fe-N-C}$ ,  $\text{Co-N-C}$ ,  $\text{Ni-N-C}$ ,  $\text{Cu-N-C}$ , and  $\text{Mn-N-C}$ ) and studied their  $\text{CO}_2\text{RR}$  performance.<sup>68</sup> The results demonstrated that  $\text{Fe-N-C}$  produced the most CO at low overpotentials, while  $\text{Ni-N-C}$  produced the most CO at high overpotentials (Fig. 6c).  $\text{Fe-N-C}$ ,  $\text{Mn-N-C}$ , and  $\text{Co-N-C}$  all bind to  $\text{CO}^{*}$  very strongly such that desorption of CO becomes the RDS for these SACs.  $\text{Ni-N-C}$  and  $\text{Cu-N-C}$  display a weak binding to  $^{*}\text{COOH}$  and thus they require higher overpotentials to initiate the  $\text{CO}_2\text{RR}$ . Interestingly, a small amount of  $\text{CH}_4$  was detected in the  $\text{CO}_2\text{RR}$  catalyzed on  $\text{Fe-N-C}$  and  $\text{Mn-N-C}$  due to their strong adsorption towards  $\text{CO}^{*}$ , indicating their potential for producing  $\text{CH}_4$  (Fig. 6d). Other studies also attained a similar consensus that the Ni SAC possessed the highest activity and selectivity for the  $\text{CO}_2\text{RR}$  to CO among different SACs.<sup>69-73</sup>

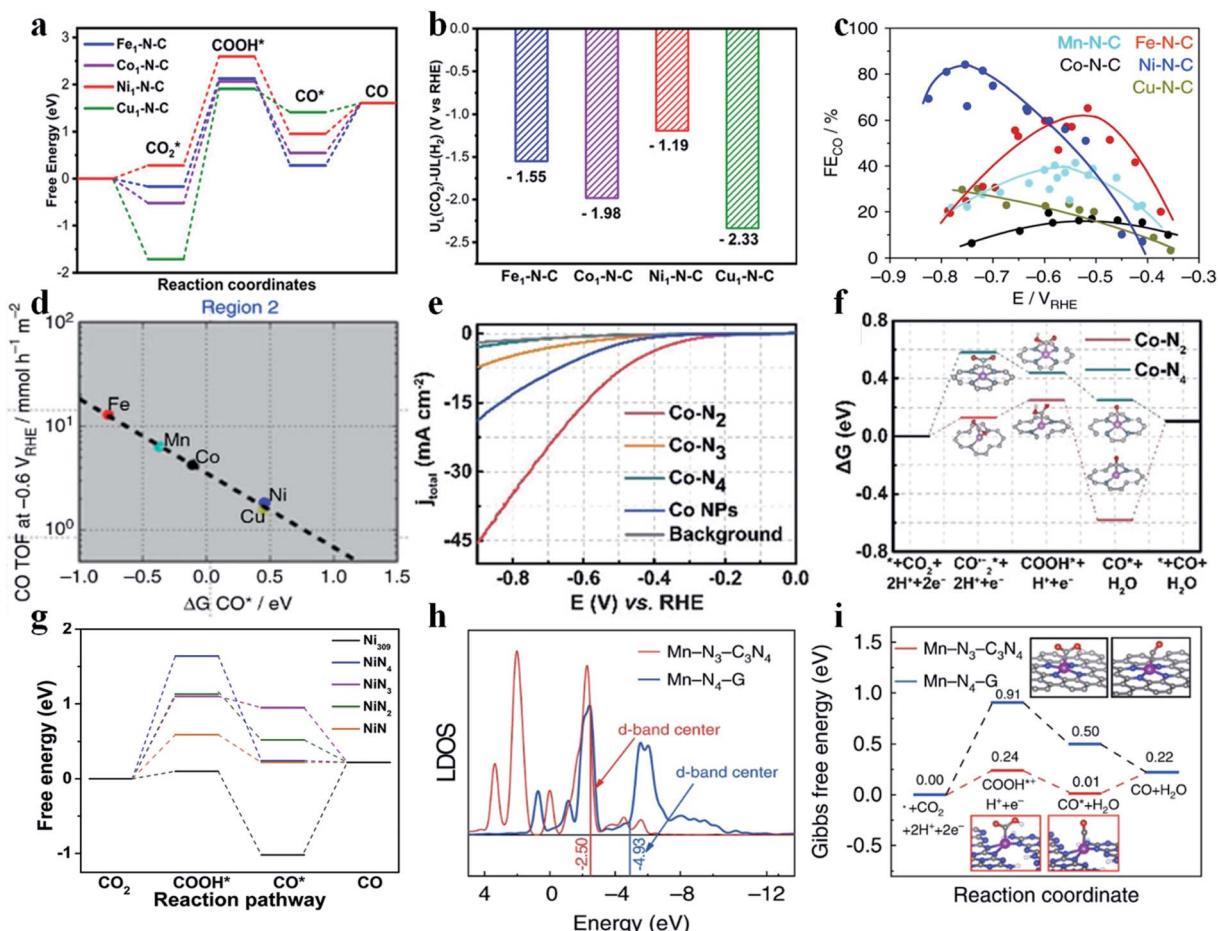


Fig. 6 (a) Calculated free energy diagram of  $\text{CO}_2$  reduction to CO and (b) the values of  $U_{\text{L}}(\text{CO}_2) - U_{\text{L}}(\text{H}_2)$  for various M1-N-C catalysts. Reproduced with permission from ref. 67. Copyright (2020) Wiley-VCH. (c)  $\text{FE}_{\text{CO}}$  for various SACs at different potentials. (d)  $\text{TOF}_{\text{CO}}$  at  $-0.6\text{ V}$  vs. RHE as a function of CO free adsorption energy. Reproduced with permission from ref. 68. Copyright (2017) Springer Nature. (e) LSV curves of  $\text{Co-N}_2$ ,  $\text{Co-N}_3$ ,  $\text{Co-N}_4$ , and Co NPs and pure carbon paper as the background. (f) Calculated Gibbs free energy diagram for  $\text{CO}_2$  electro-reduction to CO on  $\text{Co-N}_2$  and  $\text{Co-N}_4$ . Reproduced with permission from ref. 74. Copyright (2018) Wiley-VCH. (g) Free energy diagram for conversion of  $\text{CO}_2$  to CO on a Ni-SAC and  $\text{Ni}_{309}$  cluster at  $U = 0\text{ V}$  vs. RHE. Reproduced with permission from ref. 76. Copyright (2019) Elsevier. (h) Local density of states (LDOS) of Mn in  $\text{Mn-N}_3\text{-C}_3\text{N}_4$  and  $\text{Mn-N}_4\text{-G}$ . (i) Calculated Gibbs free energy diagram for the  $\text{CO}_2\text{RR}$  over  $\text{Mn-N}_3\text{-C}_3\text{N}_4$  and  $\text{Mn-N}_4\text{-G}$ . Reproduced with permission from ref. 77. Copyright (2020) Springer Nature.

**3.2.2. Effect of coordination number on  $\text{CO}_2$  reduction to CO.** Typically, in SACs, the metal atomic center is coordinated with four non-metal atoms. However, this structure does not always give the best  $\text{CO}_2$ RR activity. Regulating the coordination number in SACs offers an effective strategy to tune the adsorption energy of reaction intermediates and thus their catalytic performance. Generally, the lower the coordination number, the stronger the adsorption of intermediates on SACs. Li *et al.* prepared  $\text{Co}-\text{N}_2$ ,  $\text{Co}-\text{N}_3$ , and  $\text{Co}-\text{N}_4$  by calcining  $\text{Co}/\text{Zn}$  zeolitic imidazolate frameworks (ZIFs) at different temperatures.<sup>74</sup> Since N species became volatile at high temperature,  $\text{Co}-\text{N}_2$ ,  $\text{Co}-\text{N}_3$ , and  $\text{Co}-\text{N}_4$  could be obtained at 1000 °C, 900 °C, and 800 °C. The atomically dispersed Co atoms could be directly observed by HAADF-STEM. EXAFS confirmed the existence of Co-N bonds (at around 1.4 Å) and the absence of Co-Co bonds. The intensity of the Co-N peak for  $\text{Co}-\text{N}_2$  was found much lower than that for  $\text{Co}-\text{N}_3$  and  $\text{Co}-\text{N}_4$ , indicating lower coordination around the Co center in  $\text{Co}-\text{N}_2$ . EXAFS fitting gave the Co-N coordination number in these Co-SACs of 2.2, 3.1, and 4.1, respectively. Electrochemical measurements showed that  $\text{Co}-\text{N}_2$  had the highest activity to reduce  $\text{CO}_2$  to CO (Fig. 6e).  $\text{Co}-\text{N}_2$ ,  $\text{Co}-\text{N}_3$ , and  $\text{Co}-\text{N}_4$  have similar structural parameters except the Co-N coordination number, and provide an ideal platform to elucidate the influence of coordination number on  $\text{CO}_2$ RR performance. DFT calculations disclosed that the endergonic  $\text{CO}_2^{\cdot-}\text{*}$  formation was the RDS for these Co-SACs. Owing to the higher d-band center of  $\text{Co}-\text{N}_2$  (−0.81 eV) than that of  $\text{Co}-\text{N}_4$  (−1.06 eV),  $\text{Co}-\text{N}_2$  had a lower energy barrier than  $\text{Co}-\text{N}_4$  to form  $\text{COO}^{\cdot-}\text{*}$ , explaining the higher  $\text{CO}_2$ RR activity on  $\text{Co}-\text{N}_2$  (Fig. 6f). Additionally, the authors further measured the  $\text{OH}^-$  adsorption strength to simulate the binding affinity of  $\text{COO}^{\cdot-}\text{*}$  as  $\text{COO}^{\cdot-}\text{*}$  was unstable in the electrolyte.  $\text{Co}-\text{N}_2$  showed a more negative  $\text{OH}^-$  adsorption peak, verifying its stronger adsorption to  $\text{COO}^{\cdot-}\text{*}$ . Considering the higher catalytic activity of  $\text{Co}-\text{N}_4$  towards the HER,<sup>75</sup> the enhanced  $\text{CO}_2$ RR performance of  $\text{Co}-\text{N}_2$  could also be related to the increase in  $U_{\text{l}}(\text{CO}_2) - U_{\text{l}}(\text{H}_2)$ . This work indicated that lower coordination number in SACs would enhance the adsorption of  $\text{CO}_2$ RR intermediates. Li *et al.* performed DFT calculations to study Ni SACs with different coordination numbers ( $\text{NiN}_x$ ;  $x = 1\text{--}4$ ) toward catalyzing the  $\text{CO}_2$ RR.<sup>76</sup> The results show that the RDS for all studied  $\text{NiN}_x$  SACs is the formation of  $\text{COOH}^{\cdot-}$  – an endergonic step. NiN has the lowest coordination number and thus possesses the smallest energy barrier to generate the  $\text{COOH}^{\cdot-}$  intermediate, justifying its highest  $\text{CO}_2$ RR activity (Fig. 6g). Zhang *et al.* synthesized  $\text{Mn}-\text{N}_3$  and  $\text{Mn}-\text{N}_4$  catalysts and measured their  $\text{CO}_2$ RR performance. The  $\text{Mn}-\text{N}_3$  catalyst delivered a 98.8% CO FE with a CO partial current density of 14 mA cm<sup>−2</sup> at an overpotential of 0.44 V. *In situ* X-ray absorption spectroscopy showed that  $\text{Mn}-\text{N}_3$  facilitated the formation of  $\text{COOH}^{\cdot-}$ , which is the RDS. DFT calculation gave an energy barrier of 0.24 eV for  $\text{Mn}-\text{N}_3$  and 0.91 eV for  $\text{Mn}-\text{N}_4$  (Fig. 6i). Local density of states (LDOS) revealed that the d-band centers of  $\text{Mn}-\text{N}_3$  and  $\text{Mn}-\text{N}_4$  were located at −2.50 eV and −4.93 eV, respectively (Fig. 6h).<sup>77</sup> Other researchers also reached a similar conclusion that the lower coordination number in SACs indeed strengthened the adsorption of  $\text{CO}_2$ RR intermediates.<sup>78–83</sup>

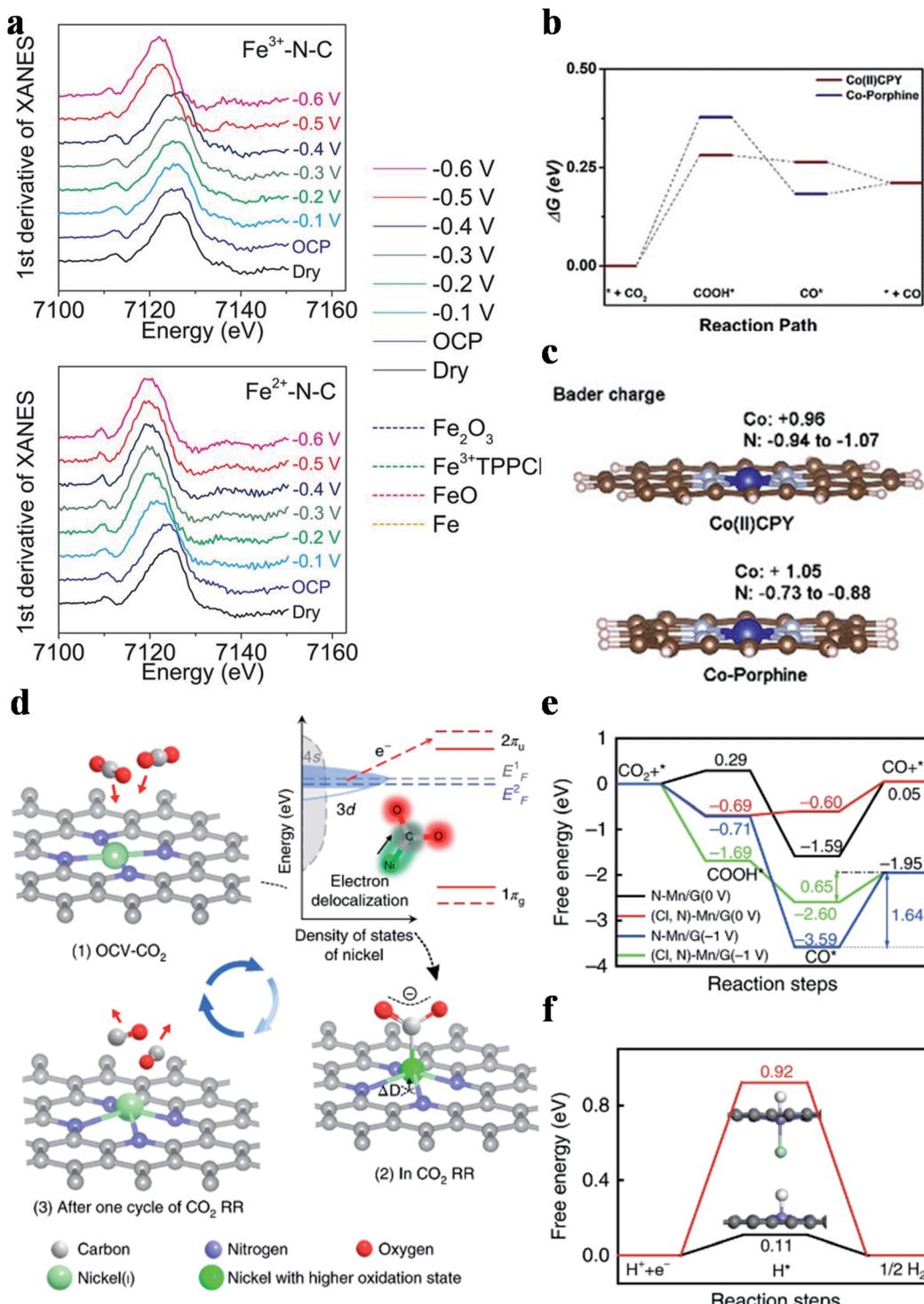
**3.2.3. Effect of the coordinated nitrogen type on  $\text{CO}_2$  reduction to CO.** Four types of nitrogen atoms exist in SACs,

namely pyridinic, pyrrolic, graphitic and oxidized N. The metal centers in SACs could be bonded with pyridinic N or pyrrolic N. The d-band center for pyrrolic-N coordinated metal sites is lower than that for pyridinic-N coordinated metal sites and thus pyrrolic-N coordinated metal sites bind to the  $\text{CO}_2$ RR intermediates more weakly. Hu *et al.* prepared  $\text{Fe}^{3+}\text{-N-C}$  coordinated with pyrrolic N and  $\text{Fe}^{2+}\text{-N-C}$  coordinated with pyridinic N using different pyrolysis precursors.<sup>84</sup>  $\text{Fe}^{3+}\text{-N-C}$  could reduce  $\text{CO}_2$  to CO with a CO partial current density of 94 mA cm<sup>−2</sup> at an overpotential of 340 mV. No catalytic performance decay was observed in 12 hours of continuous reaction. *Operando* X-ray absorption spectroscopy verified the true active sites of  $\text{Fe}^{3+}$  ions coordinated with pyrrolic N atoms and the +3 oxidation state of Fe was maintained during the reaction (Fig. 7a). Furthermore, electrochemical measurements indicated that the faster  $\text{CO}_2$  activation and weaker CO adsorption were responsible for the superior catalytic activity of  $\text{Fe}^{3+}\text{-N-C}$ . Other research groups also regarded M-pyrrolic N as the active center for the  $\text{CO}_2$ RR.<sup>85,86</sup> Wang *et al.* constructed  $\text{Co}(\text{II})\text{CPY}$  (Co atoms coordinated with four pyridinic N atoms) and Co-porphine (Co atoms coordinated with four pyrrolic N atoms) and found that  $\text{Co}(\text{II})\text{CPY}$  showed better  $\text{CO}_2$ RR activity than Co-porphine.<sup>87</sup> DFT calculations suggested that the formation of  $\text{COOH}^{\cdot-}$  was the RDS, in which  $\text{Co}(\text{II})\text{CPY}$  had a lower energy barrier (Fig. 7b). Bader charge analysis showed that the Co atoms in  $\text{Co}(\text{II})\text{CPY}$  could get more electrons from the ligand compared with the case in Co-porphine (Fig. 7c). Projected density of states (PDOS) demonstrated that the  $d_{z^2}$  orbital of  $\text{Co}(\text{II})\text{CPY}$  was closer to the Fermi level before the reaction and had a larger overlap with the 2p orbital of COOH after the reaction, substantiating the enhancement of  $\text{COOH}^{\cdot-}$  adsorption in  $\text{Co}(\text{II})\text{CPY}$ . Other research studies also reached the same conclusion that M-pyridinic N species served as the reaction sites in catalyzing the  $\text{CO}_2$ RR.<sup>72,73,88–91</sup> Since the controversy about which type of M-N species is the active site(s) in the  $\text{CO}_2$ RR still remains, more attention has to be paid on this research hotspot.

#### 3.2.4. Effect of heteroatoms on $\text{CO}_2$ reduction to CO.

Heteroatom doping could induce electron transfer between the metal atomic center and the surrounding non-metal atoms, leading to the distinct electronic structure and hence the electrocatalytic performance. Liu *et al.* synthesized a S doped Ni-SAC ( $\text{Ni}-\text{N}_3\text{S}$ ) and  $\text{Ni}-\text{N}_4$  and studied their  $\text{CO}_2$ RR mechanisms.<sup>92</sup> The  $\text{CO}_2$ RR onset potential of  $\text{Ni}-\text{N}_3\text{S}$  was 100 mV lower than that of  $\text{Ni}-\text{N}_4$ . *Operando* XAS showed that the valence state of Ni atoms in Ni SACs was +1, serving as the true active sites. Moreover, the  $\text{Ni}^+$  sites were identified as having strong interactions with  $\text{CO}_2$ , where electrons were transferred from  $\text{Ni}^+$  to the C 2p orbital in  $\text{CO}_2$  to generate  $\text{CO}_2^{\cdot-}$ , facilitating the  $\text{CO}_2$  activation and further reduction (Fig. 7d). Consequently, the catalyst achieved a specific current of 350 A g<sub>catalyst</sub><sup>−1</sup> and a TOF of 14 800 h<sup>−1</sup> at an overpotential of 0.61 V with 97% FE<sub>CO</sub>. The authors also proposed the activation process of  $\text{CO}_2$  on the Ni(i) active center and its structural evolution during the  $\text{CO}_2$ RR (Fig. 7d). Cl doping in a Mn-SAC was reported by Zhang *et al.* to improve the  $\text{CO}_2$ RR activity. Mn-SACs usually displayed poor selectivity towards CO production because of their too strong adsorption for  $\text{CO}^*$ , making CO release rather difficult. After





**Fig. 7** (a) The first derivative of the XANES spectra for Fe<sup>3+</sup>-N-C and Fe<sup>2+</sup>-N-C as dry powder (black) and on a glassy carbon electrode at the open circuit potential (OCP) (blue), -0.1 V (light blue), -0.2 V (green), -0.3 V (dark green), -0.4 V (dark blue), -0.5 V (red), and -0.6 V (pink) versus RHE, with Fe<sub>2</sub>O<sub>3</sub> (blue dashed), Fe<sup>3+</sup>TPPCL (green dashed), FeO (pink dashed), and Fe foil (orange dashed) references. Reproduced with permission from ref. 84. Copyright (2019) the American Association for the Advancement of Science. (b) Free energy profiles of Co(II)CPY/ graphene and Co-porphine/graphene. (c) Bader charge of Co and N atoms. Reproduced with permission from ref. 87. Copyright (2020) Wiley-VCH. (d) Structural evolution of the active sites in electrochemical CO<sub>2</sub> reduction. Reproduced with permission from ref. 92. Copyright (2018) Springer Nature. (e) Calculated free energy of the CO<sub>2</sub>RR. (f) Calculated free energy of hydrogen adsorption. Reproduced with permission from ref. 93. Copyright (2019) Springer Nature.

introducing Cl into the Mn-SAC ((Cl, N)-Mn/G), the selectivity towards CO was significantly increased from 17% to 97% with the partial current density for CO production exhibiting an 11-fold increase. PDOS revealed that the d-band center of (Cl, N)-Mn/G was lower than that of MnN<sub>4</sub>, weakening the CO\* adsorption and thus improving the CO selectivity. The free energy diagram further supported this conclusion. Specifically, the energy barrier of the RDS (desorption of CO\*) decreased from 1.64 eV for MnN<sub>4</sub> to 0.65 eV for (Cl, N)-Mn/G (Fig. 7e). Moreover, the energy barrier for H<sub>2</sub> generation increased from 0.11 eV for MnN<sub>4</sub> to 0.92 eV for (Cl, N)-Mn/G, implying that the HER was largely suppressed (Fig. 7f).<sup>93</sup>

### 3.2.5. Effect of dual metal atoms on CO<sub>2</sub> reduction to CO.

Although much progress has been made in the CO<sub>2</sub>RR to

produce CO using SACs, their performance could be further improved through constructing dual metal atomic sites. Gong *et al.* demonstrated an example of neighboring Zn and Co monomers (ZnCoNC) for enhancing CO production in the CO<sub>2</sub>RR.<sup>94</sup> ZnCoNC displayed a CO FE of 93.2% at  $-0.5$  V vs. RHE in 30 h. XANES confirmed the interaction between Zn and Co. According to the free energy diagram, after introducing Co into the Zn-SAC, the formation of COOH\* (the RDS for the Zn-SAC) changed from endergonic to exergonic (Fig. 8a), which enhanced the adsorption of COOH\* and thus promoted CO production. Zhao *et al.* synthesized a Ni-Fe dual-metal-atom catalyst (NiFe-N-C).<sup>95</sup> Electrochemical study disclosed that NiFe-N-C possessed higher activity and selectivity than Ni-N-C and Fe-N-C in the CO<sub>2</sub>RR (Fig. 8b and c). The calculated free

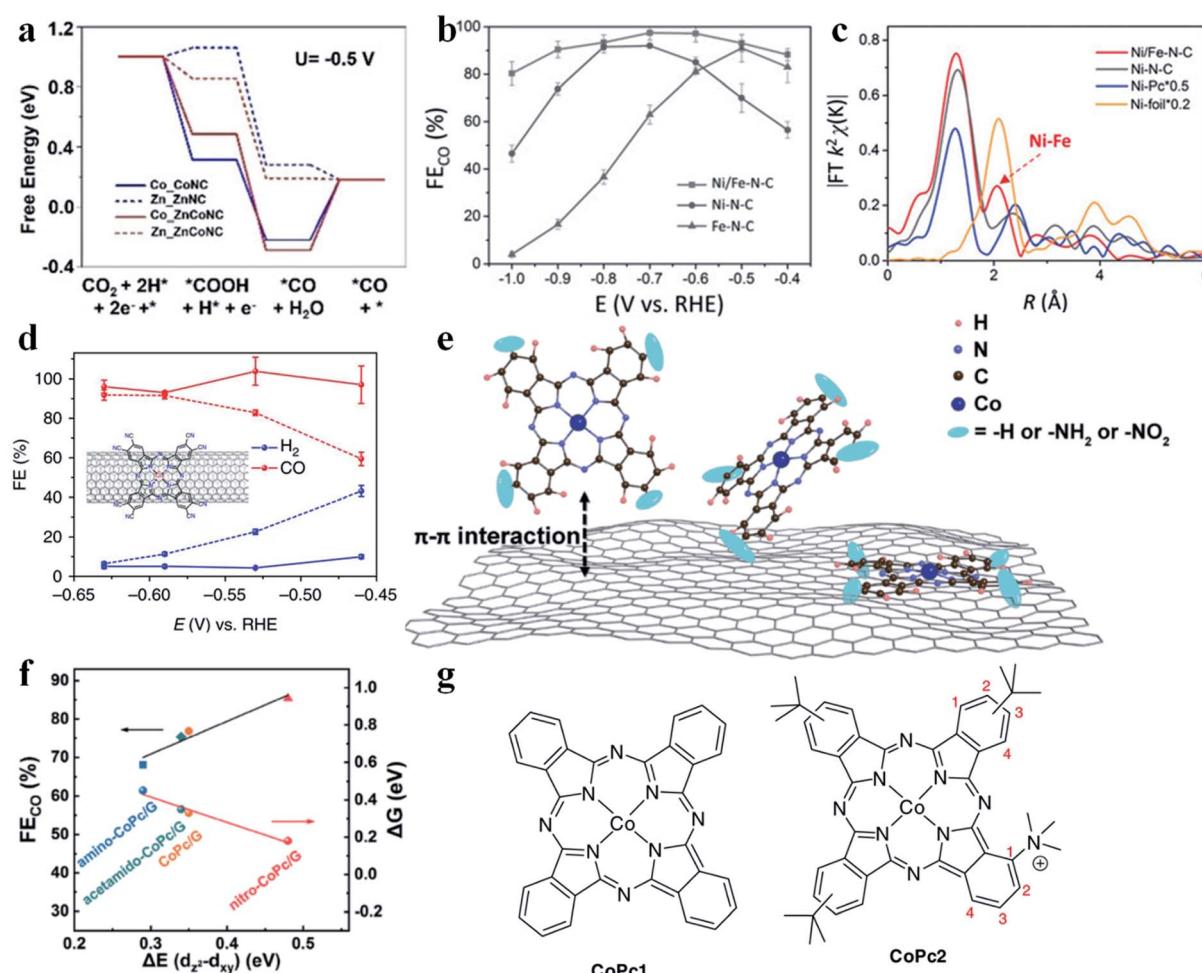


Fig. 8 (a) Calculated free energy for CO<sub>2</sub> reduction to CO. Reproduced with permission from ref. 94. Copyright (2020) Wiley-VCH. (b) FE of CO for various SACs. (c) Fourier transformation of the EXAFS spectra at R space. Reproduced with permission from ref. 95. Copyright (2019) Wiley-VCH. (d) Faradaic efficiencies of reduction products at different potentials for CoPc-CN/CNT (solid line) in comparison with CoPc/CNT (dotted line). The inset in (d) shows the molecular structure of CoPc-CN, which is anchored on a CNT. The average values and error bars in (e) are based on six measurements during three reaction runs (two product analysis measurements were performed in each run). The error bars represent standard deviation of six measurements. The data are all iR corrected. Reproduced with permission from ref. 97. Copyright (2017) Springer Nature. (e) Schematic illustration showing the construction of single cobalt atom catalysts for the CO<sub>2</sub>RR. (f) The linear relationship between the CO faradaic efficiency/Gibbs free energy of CO<sub>2</sub> reduction to the \*CO<sub>2</sub><sup>-</sup> intermediate and the energy difference  $\Delta E(d_{z^2} - d_{xy})$ . Reproduced with permission from ref. 96. Copyright (2020) Springer. (g) CoPc1 (left) bears no substituents, and CoPc2 (right) bears one trimethyl ammonium group at position 1 of the isoindole subunits, and three *tert*-butyl groups (position 2 or 3) of the other subunits. Reproduced with permission from ref. 98. Copyright (2019) Springer Nature.



energy diagram showed that the energy barrier for  $\text{COOH}^*$  formation (RDS) was much lower in NiFe-N-C than in Ni-N-C. Therefore, Fe doping could strengthen the binding affinity of Ni atoms for  $\text{COOH}^*$ . It is worth mentioning that two mechanisms are possible for enhancing the  $\text{CO}_2\text{RR}$  performance in dual metal atom catalysts. One is that only one metal site acts as the active center, and the introduction of the second metal atom regulates the electronic structure of the first metal site. The other is that both metal sites serve as the active centers for adsorbing reaction intermediates and engage in the reaction. To date, the reported examples belong to the former mechanism. If the reaction could follow the latter mechanism on dual metal atom catalysts, the scaling relationship might be broken, which provides another possibility to tune the  $\text{CO}_2\text{RR}$  performance.

### 3.2.6. Effect of surrounding functional groups on $\text{CO}_2$ reduction to CO. The charge state of the metal atomic center

determines its intrinsic catalytic activity. Therefore, introducing functional groups (electron-withdrawing or electron-donating) into SACs offers an effective strategy to manipulate their  $\text{CO}_2\text{RR}$  performance. Huang *et al.* prepared CoPc/G, amino functionalized CoPc/G (amino-CoPc/G), and nitro functionalized CoPc/G (nitro-CoPc/G) and studied the effect of electron-withdrawing/electron-donating groups in SACs on the  $\text{CO}_2\text{RR}$  activity (Fig. 8e).<sup>96</sup> Electrochemical measurements showed that nitro-CoPc/G possessed the highest activity and selectivity for generating CO. DFT calculations revealed that formation of  $^*\text{CO}_2^-$  was the RDS, where nitro-CoPc/G had the lowest energy barrier. After the introduction of the electron-withdrawing nitro group, the electron density around the Co site decreased. Also, the  $d_{z^2}$  orbital was upshifted and became less affected by other lower energy level orbitals, like  $d_{xy}$ . Another important descriptor was also found, that is, the larger the energy difference between the  $d_{z^2}$  and  $d_{xy}$  orbital, the smaller the energy

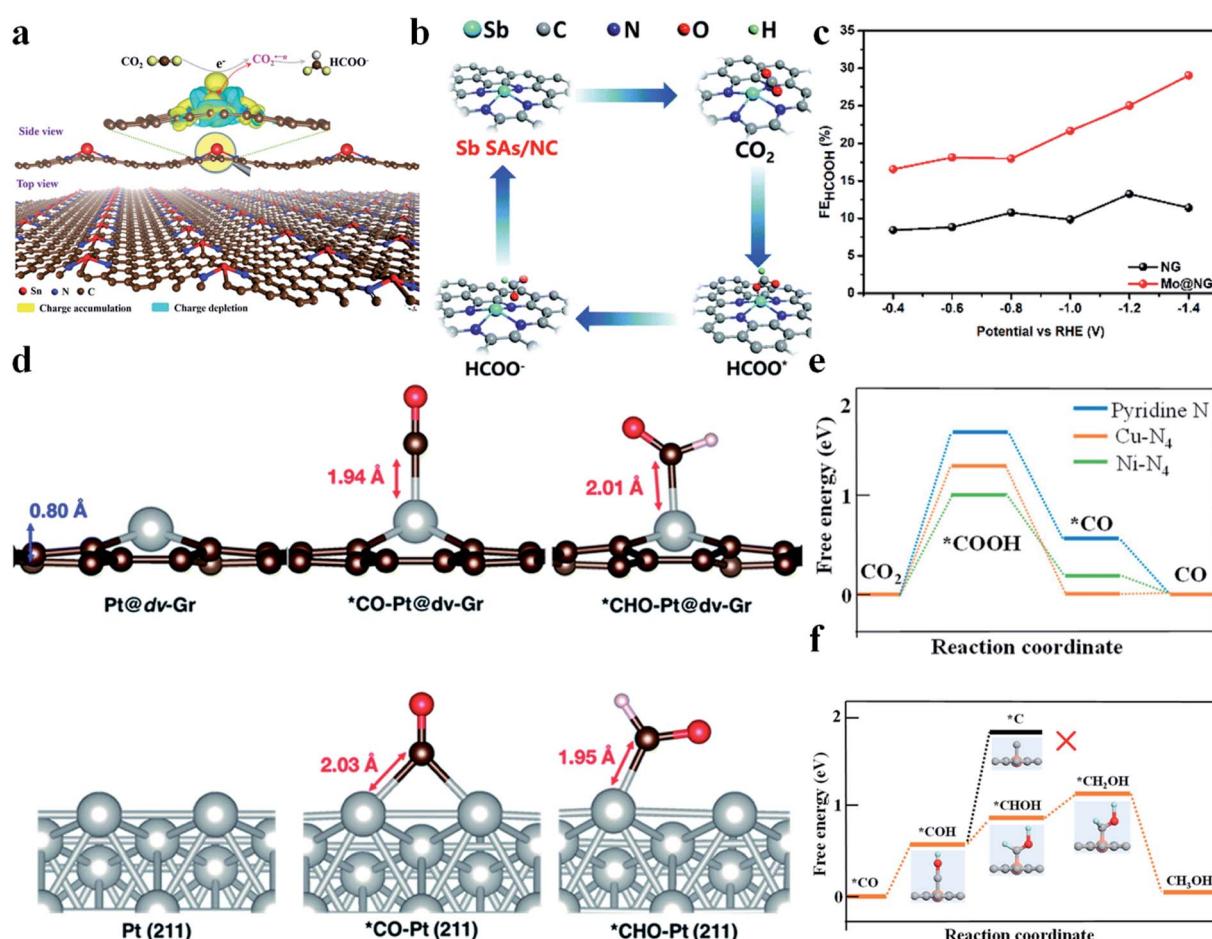


Fig. 9 (a) Plot showing 3D differential charge density of single  $\text{Sn}^{\delta+}$  atoms on N-doped graphene and the schematic illustration of  $\text{CO}_2$  electroreduction into formate. The yellow and blue isosurfaces correspond to the increase and depletion in the number of electrons, respectively. Reproduced with permission from ref. 99. Copyright (2019) Wiley-VCH. (b) Proposed  $\text{CO}_2\text{RR}$  mechanism on Sb SA/NC. Reproduced with permission from ref. 101. Copyright (2020) The Royal Society of Chemistry. (c) Comparison of formate faradaic efficiency between NG and Mo@NG. Reproduced with permission from ref. 102. Copyright (2019) Elsevier. (d) Optimized geometries of Pt@dv-Gr and Pt (211) before and after adsorption of  $^*\text{CO}$  and  $^*\text{CHO}$ . Reproduced with permission from ref. 7. Copyright (2017) The Royal Society of Chemistry. (e) Free energy diagram of  $\text{CO}_2$  reduction to CO on pyridine N, Ni-N<sub>4</sub>, and Cu-N<sub>4</sub>. Orange, gray, dark blue, red, and light blue spheres stand for Cu, C, N, O, and H atoms, respectively. Reproduced with permission from ref. 105. Copyright (2019) American Chemical Society.



barrier to form  $^*\text{CO}_2^-$  (Fig. 8f). Wang *et al.* introduced an electron-withdrawing cyano group into CoPc/CNT (CoPc-CN/CNT) and found that both activity and CO selectivity increased obviously (Fig. 8d).<sup>97</sup> The electron-withdrawing cyano group could prompt the generation of Co(i), which was regarded as the active site for the  $\text{CO}_2\text{RR}$ . The enhanced Co(II)/Co(i) redox transition at more positive potentials in CoPc-CN/CNT supported this proposal. Moreover, the cyano group also reduced the affinity of the Co site for  $\text{CO}^*$ , facilitating the release of CO. In addition to the nitro group and cyano group, a trimethyl ammonium group (CoPc2) was also introduced into CoPc1 (Fig. 8g).<sup>98</sup> After such a modification, the CoPc2 showed high selectivity towards CO production, while the CO partial current density increased substantially.

### 3.3. HCOOH

It is reported that SACs with a p-block metal (Sn, Sb) center are able to catalyze the  $\text{CO}_2\text{RR}$  to produce formic acid or formate. Xie *et al.* synthesized  $\text{SnN}_2\text{C}_2$  and found that it could reduce  $\text{CO}_2$  to formate at a very low onset overpotential of 60 mV and with a high TOF of  $11\,930\text{ h}^{-1}$  at  $-1.14\text{ V vs. RHE}$ .<sup>99</sup> Moreover, its activity did not decay during 200 h of continuous reaction. DFT calculations revealed that electrons were transferred from Sn atoms to graphene, making Sn atoms positively charged. Fourier transformed infrared spectroscopy (FTIR) spectra and Gibbs free energy calculations confirmed that  $\text{Sn}^{\delta+}$  could facilitate  $\text{CO}_2$  activation and protonation through stabilizing  $\text{CO}_2^{*-}$  and  $\text{HCOO}^*$  (Fig. 9a). Wei *et al.* constructed a NiSn atomic pair (NiSn-APC) and also achieved a good performance in the  $\text{CO}_2\text{RR}$  to formate.<sup>100</sup> NiSn-APC produced HCOOH with a high TOF of  $4752\text{ h}^{-1}$  and formate productivity of  $36.7\text{ mol h}^{-1}\text{ g}_{\text{Sn}}^{-1}$  at  $-1.02\text{ V vs. RHE}$ . *In situ* attenuated total reflection-infrared (ATR-IR) spectra and theoretical calculations confirmed the electron redistribution on Sn, which is induced by the adjacent Ni atoms. Moreover,  $\Delta G$  ( $^*\text{HCOOH}$ ) ( $-0.05\text{ eV}$ ) was much smaller than  $\Delta G$  ( $^*\text{COOH}$ ) ( $1.36\text{ eV}$ ), explaining its high selectivity towards formate production. Sb-N<sub>4</sub> (Sb SA/NC) reported by Li's group also displayed a good  $\text{CO}_2\text{RR}$  performance.<sup>101</sup> Sb SA/NC produced formate with a FE of 94% at  $-0.8\text{ V vs. RHE}$ . *In situ* XAFS and DFT calculations verified that the positively charged  $\text{Sb}^{\delta+}\text{-N}_4$  was the origin of the high catalytic activity. Sb SA/NC possessed a  $\Delta G$  ( $\text{HCOO}^*$ ) ( $0.21\text{ eV}$ ) smaller than  $\Delta G$  ( $\text{COOH}^*$ ) ( $1.00\text{ eV}$ ) and  $\Delta G$  ( $\text{H}^*$ ) ( $0.81\text{ eV}$ ), implying that formate production was more favorable than CO and  $\text{H}_2$  (Fig. 9b). Xie *et al.* reported that Mo atoms supported on N doped graphene (Mo@NG) could also efficiently reduce  $\text{CO}_2$  to produce HCOOH. Mo@NG generated HCOOH with a high FE, twice as that of NG, and achieved a formate yield of  $747\text{ mmol g}_{\text{catalyst}}^{-1}\text{ h}^{-1}$  (Fig. 9c).<sup>102</sup>

### 3.4. $\text{CH}_3\text{OH}$

$\text{CH}_3\text{OH}$  is a high value-added product in the  $\text{CO}_2\text{RR}$ . However, as discussed above, both  $\text{CO}_2\text{RR}$  pathways to generate  $\text{CH}_3\text{OH}$  ( $^*\text{CH}_2\text{OH}$  and  $^*\text{CH}_3\text{O}$ ) possess very high energy barriers and thus its production remains a big challenge. Wang *et al.* immobilized cobalt phthalocyanine (CoPc) onto carbon

nanotubes (CNTs), denoted as CoPc/CNT.<sup>103</sup> CoPc/CNT was found to be able to reduce  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$  with a FE of 44% and a partial current density greater than  $10\text{ mA cm}^{-2}$  at  $-0.94\text{ V vs. RHE}$ . But the catalytic activity of CoPc/CNT quickly decayed after 1 h of electrochemical reaction. To enhance the stability, an amino functional group was introduced into CoPc/CNT to form CoPc-NH<sub>2</sub>/CNT, whose stability was greatly improved. In addition to experiments, theoretical studies have also been conducted to prompt the discovery of potential catalysts to reduce  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$ . Cai *et al.* anchored Co, Rh, and Ir atoms onto porphyrin-like graphene.<sup>104</sup> First, the structural stability of the SACs was confirmed from the strong hybridization between metal d-orbitals and N 2p-orbitals. Then, the energy barriers for the  $\text{CO}_2\text{RR}$  to  $\text{CH}_3\text{OH}$  were calculated. CoN<sub>4</sub>/graphene was found most promising among the three studied catalysts for  $\text{CH}_3\text{OH}$  generation with a RDS energy barrier of only  $0.59\text{ eV}$ . Jung *et al.* conducted DFT calculations to predict a series of transition metal SACs on graphene with single and double vacancies.<sup>7</sup> They figured out that Ni and Pt SACs with double vacancies (Ni@dv-Gr, Pt@dv-Gr) were promising to reduce  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$ . Taking Pt@dv-Gr as an example,  $\text{CO}^*$  was adsorbed on one Pt atom *via* the top-on adsorption configuration, while bulk Pt adsorbed  $\text{CO}^*$  *via* two Pt atoms adopting the bridge adsorption mode. As a result, bulk Pt adsorbed  $\text{CO}^*$  so strongly that the transformation of  $\text{CO}^*$  to  $^*\text{CHO}$  – an important intermediate for  $\text{CH}_3\text{OH}$  formation – became rather difficult. In contrast, Pt@dv-Gr had a much smaller energy barrier for this step and held the premise for  $\text{CH}_3\text{OH}$  production (Fig. 9d). He *et al.* developed a simple method to prepare a Cu-SAC on through-hole carbon nanofibers (Cu SAs/TCNFs).<sup>105</sup> The Cu SAs/TCNFs (Cu-N<sub>4</sub>) could generate methanol with a FE of 44%. DFT calculations found that the energy barrier for  $\text{COOH}^*$  formation was much larger than that for  $\text{CHOH}^*$  formation on Cu-N<sub>4</sub>, which effectively suppressed the CO production. Moreover, Cu-N<sub>4</sub> could adsorb  $\text{CO}^*$  more strongly than Ni-N<sub>4</sub>, which allowed  $\text{CO}^*$  to be further reduced (Fig. 9e). Additionally, the energy barrier to form  $\text{C}^*$  from  $\text{COH}^*$ , an important step towards  $\text{CH}_4$ , was calculated to be  $1.88\text{ eV}$ , which is much larger than that to form  $\text{CH}_3\text{OH}$  (Fig. 9f). Therefore,  $\text{CH}_3\text{OH}$  was more favorable than  $\text{CH}_4$  in the  $\text{CO}_2\text{RR}$ . In summary, the mechanism of the  $\text{CO}_2\text{RR}$  to form  $\text{CH}_3\text{OH}$  on SACs was nearly completely based on DFT calculation. The lack of understanding of the structural characteristics poses a big challenge for designing efficient SACs for reducing  $\text{CO}_2$  to  $\text{CH}_3\text{OH}$ .

### 3.5. $\text{CH}_4$

$\text{CH}_4$  is another important product in the  $\text{CO}_2\text{RR}$ , which undergoes an  $8\text{e}^-$  transfer process. Strong adsorption affinity of metal sites for the  $\text{CO}^*$  intermediate is required for generating  $\text{CH}_4$ . Xin *et al.* reported Zn-N<sub>4</sub> that could stably reduce  $\text{CO}_2$  to  $\text{CH}_4$  with a FE of 85% and a partial current density of  $-31.8\text{ mA cm}^{-2}$  at  $-1.8\text{ V vs. the saturated calomel electrode (SCE)}$  (Fig. 10a-c).<sup>106</sup> DFT calculations showed that Zn atoms tended to bond with O atoms to form  $^*\text{OCHO}$  ( $\Delta G$  ( $^*\text{OCHO}$ ) =  $0.46\text{ eV}$ ) rather than with C atoms to form  $\text{COOH}^*$  ( $\Delta G$  ( $^*\text{COOH}$ ) =  $1.2\text{ eV}$ ) (Fig. 10d). Furthermore, surface-enhanced infrared

absorption spectroscopy enabled direct observation of the existence of  $^*\text{OCH}_3$  and  $^*\text{OCH}_2$ . Zheng *et al.* deposited Cu atoms on  $\text{CeO}_2$  nanorods ( $\text{Cu}-\text{CeO}_2$ ), where Cu atoms were stabilized by three oxygen vacancies.  $\text{Cu}-\text{CeO}_2$  could reduce  $\text{CO}_2$  into  $\text{CH}_4$  with a FE of 58% (Fig. 10e and f).<sup>107</sup> Theoretical calculations revealed that the synergistic effect between atomic dispersion of Cu and multiple surrounding oxygen vacancies as well as the contribution from the  $\text{CeO}_2$  framework expedited  $\text{CO}_2$  adsorption and activation.

### 3.6. $\text{C}_{2+}$

Generation of  $\text{C}_{2+}$  products in the  $\text{CO}_2\text{RR}$  requires C-C coupling, which possesses a high energy barrier and is difficult to take place in SACs. Cu nanoparticles have been shown as an

excellent catalyst to reduce  $\text{CO}_2$  to form  $\text{C}_{2+}$  products, while this is not the case for Cu SACs due to the lack of neighbouring active sites to allow for C-C coupling. Fontecave *et al.* reported that a Cu SAC ( $\text{Cu}_{0.5}\text{NC}$ ) could reduce  $\text{CO}_2$  to ethanol with a FE of 43% at  $-1.2$  V vs. RHE in  $0.1$  M  $\text{CsHCO}_3$  solution.<sup>108</sup> A higher  $\text{FE}_{\text{ethanol}}$  ( $\sim 66\%$ ) could be achieved using CO as the feed gas, suggesting that  $\text{CO}^*$  might be the important intermediate to form ethanol. *Operando* XAS analysis showed that the initial isolated Cu atoms would aggregate and form Cu NPs during the  $\text{CO}_2\text{RR}$ , acting as the true active sites. Interestingly, Cu atoms could be recovered after the reaction, indicating that such a transition was reversible. Xu *et al.* also observed a similar phenomenon where Cu atoms transformed into  $\text{Cu}_n$  clusters ( $n = 3$  and 4) during the electrochemical reaction and then returned back to their initial state after the reaction.<sup>109</sup> Chen

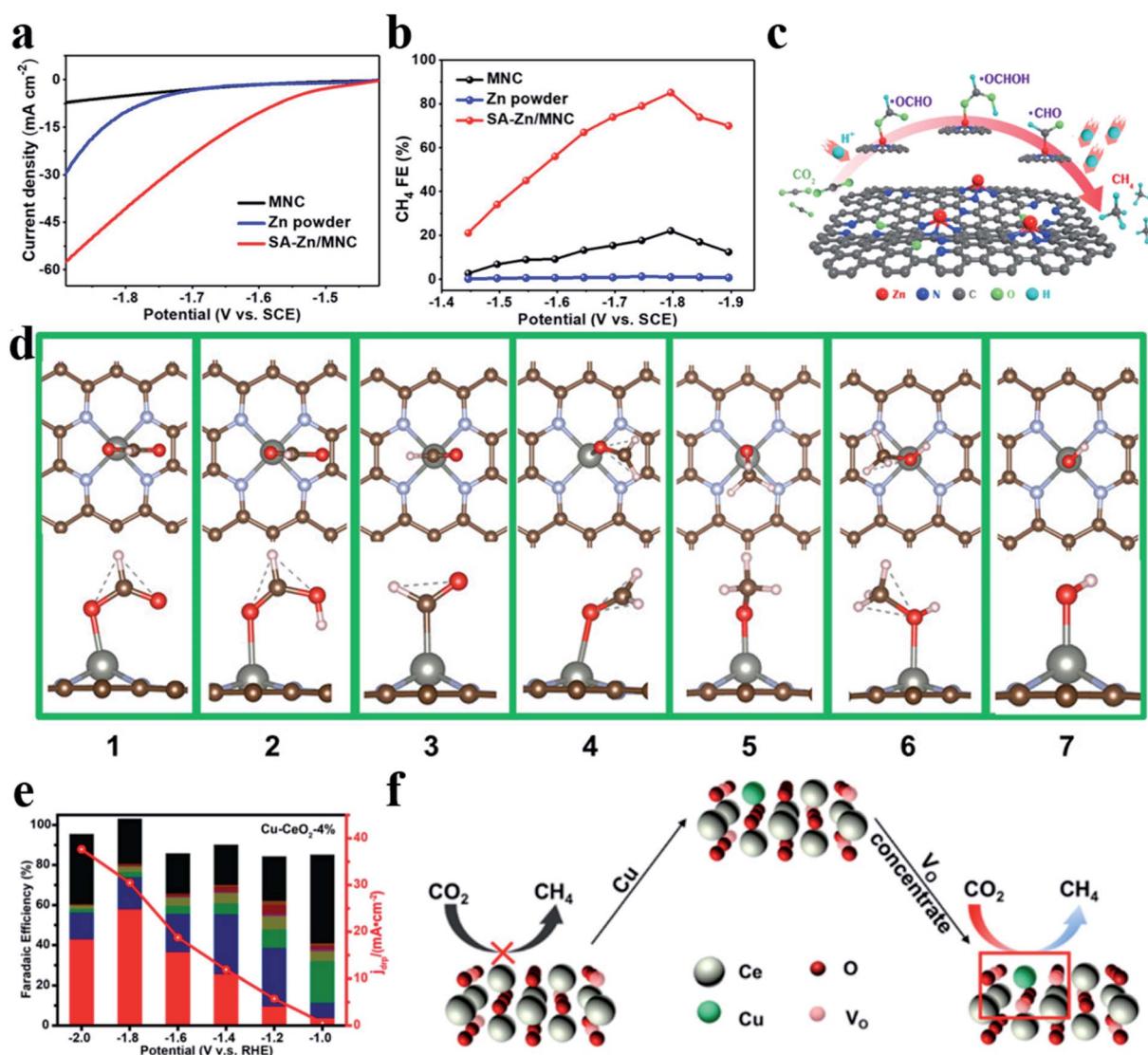


Fig. 10 (a) Polarization curves for MNC, Zn powder, and SA-Zn/MNC. (b) FE for the electrochemical  $\text{CO}_2\text{RR}$  to  $\text{CH}_4$  at different applied potentials. (c)  $\text{CO}_2\text{RR}$  pathway for single Zn atoms to produce  $\text{CH}_4$ . (d) The most stable structure. The red and pink balls represent O and H atoms, respectively. Reproduced with permission from ref. 106. Copyright (2020) American Chemical Society. (e) Faradaic efficiencies (bars, left y-axis) and the deep reduction product current density ( $j_{\text{drop}}$ , red curve, right y-axis) of  $\text{Cu}-\text{CeO}_2$ -4%. The red column represents  $\text{CH}_4$ . (f) Effect of oxygen vacancies on the  $\text{CO}_2\text{RR}$ . Reproduced with permission from ref. 107. Copyright (2018) American Chemical Society.



*et al.* designed a Cu SAC loaded on N-doped porous carbon (Cu-SA/NPC) to reduce  $\text{CO}_2$  into  $\text{C}_{2+}$  products.<sup>110</sup> Cu-SA/NPC produced acetone with a FE of 36.7% and a yield of 336.1  $\mu\text{g h}^{-1}$  at  $-0.36$  V vs. RHE. Theoretical calculations pointed out that Cu coordinated with four pyrrolic N atoms was the true active center, which decreased the energy barrier of  $\text{CO}_2$  activation and C-C coupling. Also, the most possible pathway to form acetone was proposed:  $\text{CO}_2 \rightarrow \text{COOH}^* \rightarrow \text{CO}^* \rightarrow \text{COCO}^* \rightarrow \text{COCOH}^* \rightarrow \text{COC}^* \rightarrow \text{COCH}^* \rightarrow \text{COCH}_2^* \rightarrow \text{COCH}_3^* \rightarrow \text{COCOCH}_3^* \rightarrow \text{COHCOCH}_3^* \rightarrow \text{CCOCH}_3^* \rightarrow \text{CHCOCH}_3^* \rightarrow \text{CH}_2\text{COCH}_3^* \rightarrow \text{CH}_3\text{COCH}_3$  (Fig. 11a). Zheng *et al.* regulated the population of Cu- $\text{N}_x$  sites on NC (Cu-N-C) by controlling the pyrolysis temperature (800 °C and 900 °C), where Cu-N-C-800 contained 4.9 mol% metal atoms and Cu-N-C-900 had 2.4 mol% metal atoms. Adjacent Cu- $\text{N}_2$  sites existed among the densely distributed Cu- $\text{N}_x$  in Cu-N-C-800, enabling C-C coupling for  $\text{C}_2\text{H}_4$  formation with a FE of 24.8% at  $-1.4$  V vs. RHE (Fig. 11b).<sup>111</sup> DFT calculations disclosed that Cu- $\text{N}_2$  bound with  $\text{CO}^*$  more strongly ( $-1.17$  eV) than Cu- $\text{N}_4$  ( $-0.19$  eV), which was favorable for  $\text{CO}^*$  to participate in the further reaction. Moreover, the adjacent Cu- $\text{N}_2$  sites possessed a much lower energy barrier for C-C coupling (0.14 eV) than the isolated Cu- $\text{N}_2$  (1.38 eV). Cu-N-C-900 with fewer neighboring Cu- $\text{N}_2$  sites generated much less  $\text{C}_2\text{H}_4$ , substantiating the important role of

the adjacent Cu- $\text{N}_2$  sites in C-C coupling. Qiao *et al.* came up with a novel dual active center mechanism to produce  $\text{C}_{2+}$  products in the  $\text{CO}_2\text{RR}$ , where Cu atoms bound with reaction intermediates having carbon as the anchoring atom ( $^*\text{COOH}$ ,  $^*\text{CO}$ , and  $^*\text{CHO}$ ) and C atoms on  $\text{C}_3\text{N}_4$  bound with reaction intermediates having oxygen as the anchoring atom ( $^*\text{OCH}_2$ ,  $^*\text{OCH}_3$ ,  $^*\text{O}$ , and  $^*\text{OH}$ ) (Fig. 11c).<sup>112</sup> The detection of various  $\text{C}_{2+}$  products validated the reaction mechanism, though the selectivity of  $\text{C}_{2+}$  products was low (Fig. 11d).

Tandem catalysis provides another efficient strategy to produce  $\text{C}_{2+}$  products *via* the  $\text{CO}_2\text{RR}$ , in which plenty of  $\text{CO}^*$  is first generated on one type of active site and it diffuses to the other type of active site, and then gets further reduced to produce  $\text{C}_{2+}$  products. Grätzel *et al.* fabricated a  $\text{Cu}_2\text{O}-\text{Ag}$  tandem catalyst.  $\text{CO}^*$  was first produced on the Ag sites and then underwent C-C coupling on the Cu sites to generate  $\text{C}_2\text{H}_4$ . *Operando* Raman spectroscopy allowed direct observation of the enhanced coverage of CH-containing intermediates (Fig. 12a).<sup>113</sup> Consequently, the partial current density of  $\text{C}_2\text{H}_4$  reached  $-18.1$  mA  $\text{cm}^{-2}$  at  $-1.05$  V vs. RHE on the CuAg catalyst, while it was  $-8.5$  mA  $\text{cm}^{-2}$  on the Cu catalyst. A similar tandem catalyst was demonstrated using Ni SAC as the CO generator.<sup>114</sup> By optimizing the loading amount of Ni-N-C, the Cu/Ni-N-C tandem electrode could reduce  $\text{CO}_2$  into  $\text{C}_{2+}$

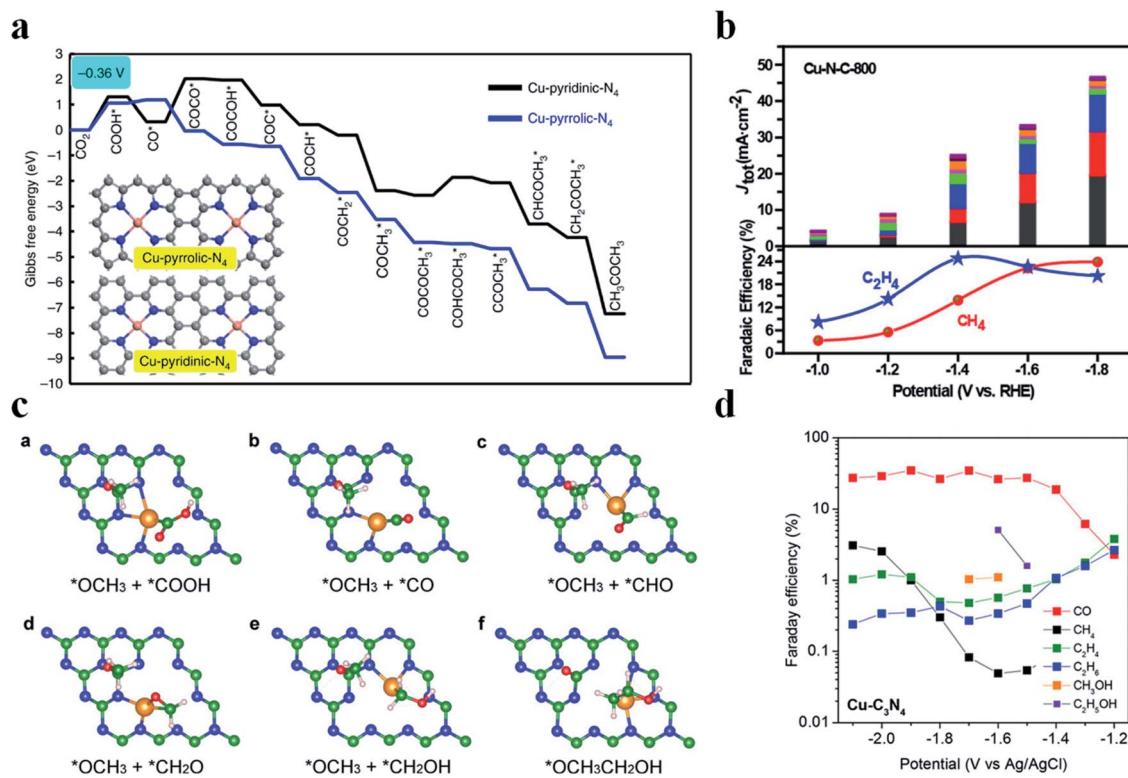


Fig. 11 (a) Free energy diagrams calculated at a potential of  $-0.36$  V vs. RHE for  $\text{CO}_2$  reduction to  $\text{CH}_3\text{COCH}_3$  on Cu-pyridinic- $\text{N}_4$  and Cu-pyrrolic- $\text{N}_4$  sites of Cu-SA/NPC (the computational models are included in the figure). Reproduced with permission from ref. 110. Copyright (2020) Springer Nature. (b)  $\text{CO}_2$  electroreduction performance of the Cu-N-C-800 catalyst. Top panel: current densities, with colors indicating different products as shown at the bottom. Bottom panel: faradaic efficiencies of  $\text{C}_2\text{H}_4$  and  $\text{CH}_4$ . Reproduced with permission from ref. 111. Copyright (2020) American Chemical Society. (c) Key reaction intermediates for  $\text{CH}_3\text{CH}_2\text{OH}$  generation on Cu- $\text{C}_3\text{N}_4$ . (d) The measured faradaic efficiencies of various products on Cu- $\text{C}_3\text{N}_4$  at different overpotentials. Reproduced with permission from ref. 112. Copyright (2017) American Chemical Society.

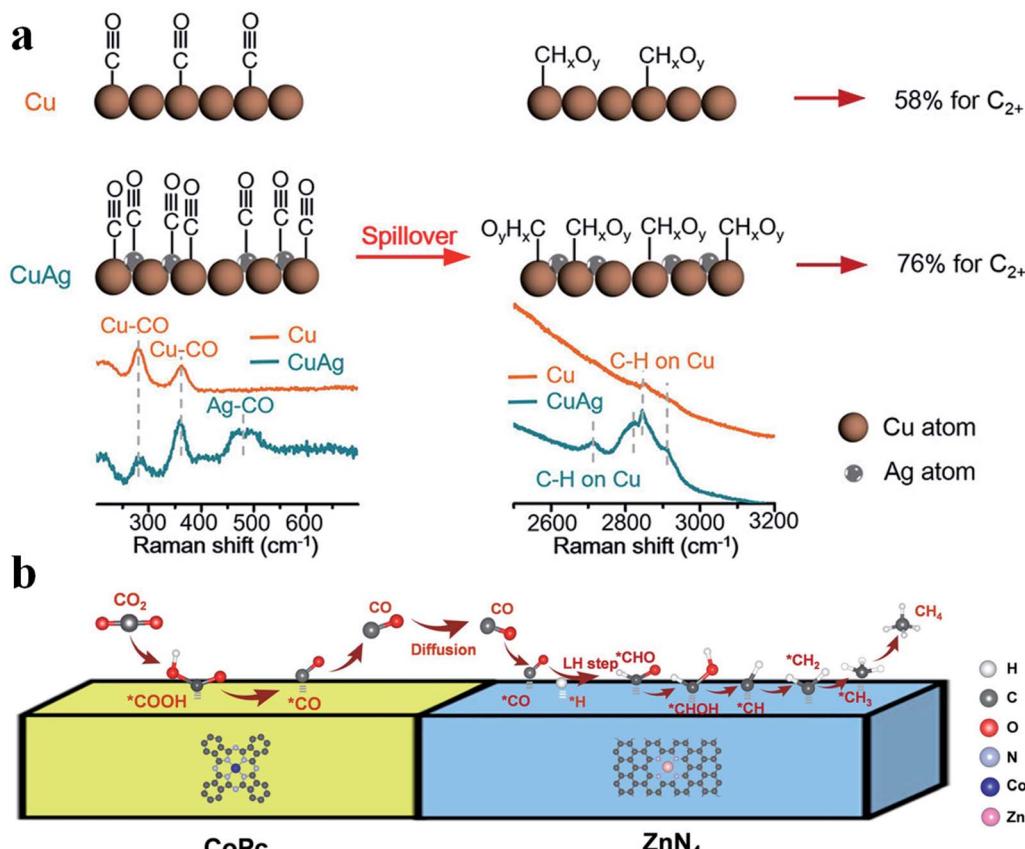


Fig. 12 (a) CO<sub>2</sub>RR mechanism for producing C<sub>2+</sub> products on Cu and CuAg catalysts. Reproduced with permission from ref. 113. Copyright (2019) American Chemical Society. (b) A proposed reaction mechanism of the CO<sub>2</sub>RR to CH<sub>4</sub> over CoPc@Zn-N-C. Reproduced with permission from ref. 116. Copyright (2020) Wiley-VCH.

products at a high production efficiency (80% FE) and rate (over 500 mA cm<sup>-2</sup>) (Fig. 13a–c).<sup>115</sup> Therefore, the tandem catalysis strategy not only efficiently promoted the C<sub>2+</sub> product faradaic efficiency, but also substantially enhanced the reaction rate. Wang *et al.* reported that CoPc@Zn-N-C was able to reduce CO<sub>2</sub> to CH<sub>4</sub> *via* a two-step tandem reaction.<sup>116</sup> CO was first generated on CoPc, and then it was further reduced to CH<sub>4</sub> on the Zn-N<sub>4</sub> site. DFT calculations disclosed that CoPc not only engaged in the first step to produce CO but also took part in the next step, where it increased the availability of H\* over nearby N sites in Zn-N<sub>4</sub> and thus benefited CH<sub>4</sub> formation (Fig. 12b). The above studies highlighted that multiple sites are essential for multi-electron product formation in the CO<sub>2</sub>RR, in which the multiple sites can be adjacent single atom sites, or metal atoms and coordination atoms.

The mechanism of the CO<sub>2</sub>RR to C<sub>2+</sub> products on Cu-based catalysts is still controversial due to the multiple electron transfer and dynamic structural transformation in the reaction. The above-mentioned challenges are also present for Cu-N-C SACs. A few studies reported that C<sub>2+</sub> could be produced by Cu-N-C SACs due to the strong adsorption of CO<sub>2</sub> reduction intermediates on Cu atoms, which is favorable for the C–C coupling. For example, some groups showed that C<sub>2+</sub> formation was catalyzed by small Cu nanoparticles or clusters in Cu-N-C

SACs, which came from aggregation of Cu single atoms under negative bias. But others reported that Cu single atoms were stable in the CO<sub>2</sub>RR, and the formation of the C<sub>2+</sub> products was on the dual active sites (Cu and N in Cu-N-C SACs). Based on the reported results, the stability of Cu-N-C SACs in the CO<sub>2</sub>RR seems to be related to the synthesis method and electrochemical reaction environment, which is directly correlated to the binding strength of Cu single atoms with the substrate. Therefore, it is crucial to develop novel strategies to enhance the binding strength between the central metal atom and the substrate for further studying the reaction mechanism of the CO<sub>2</sub>RR to C<sub>2+</sub> products on SACs. Right now, besides the Cu-N-C SAC, there are no other reported SACs capable of reducing CO<sub>2</sub> to form C<sub>2+</sub> products. As Zn and Co could strongly adsorb CO<sub>2</sub>RR intermediates, combining Zn and Co together to develop a Zn and Co diatomic catalyst might facilitate the reduction of CO<sub>2</sub> to form C<sub>2+</sub> products.

SACs supported on metals belong to single-atom alloys and some reviews have already summarized their progress.<sup>117,118</sup> Here, we focus on SACs supported on carbon-based substrates. Besides carbon, other substrates have also been used to support metal single atoms. For example, Li *et al.* deposited Ag single atoms on MnO<sub>2</sub> and found that Ag single atoms in Ag<sub>1</sub>/MnO<sub>2</sub> had a higher electronic density close to the Fermi level than Ag

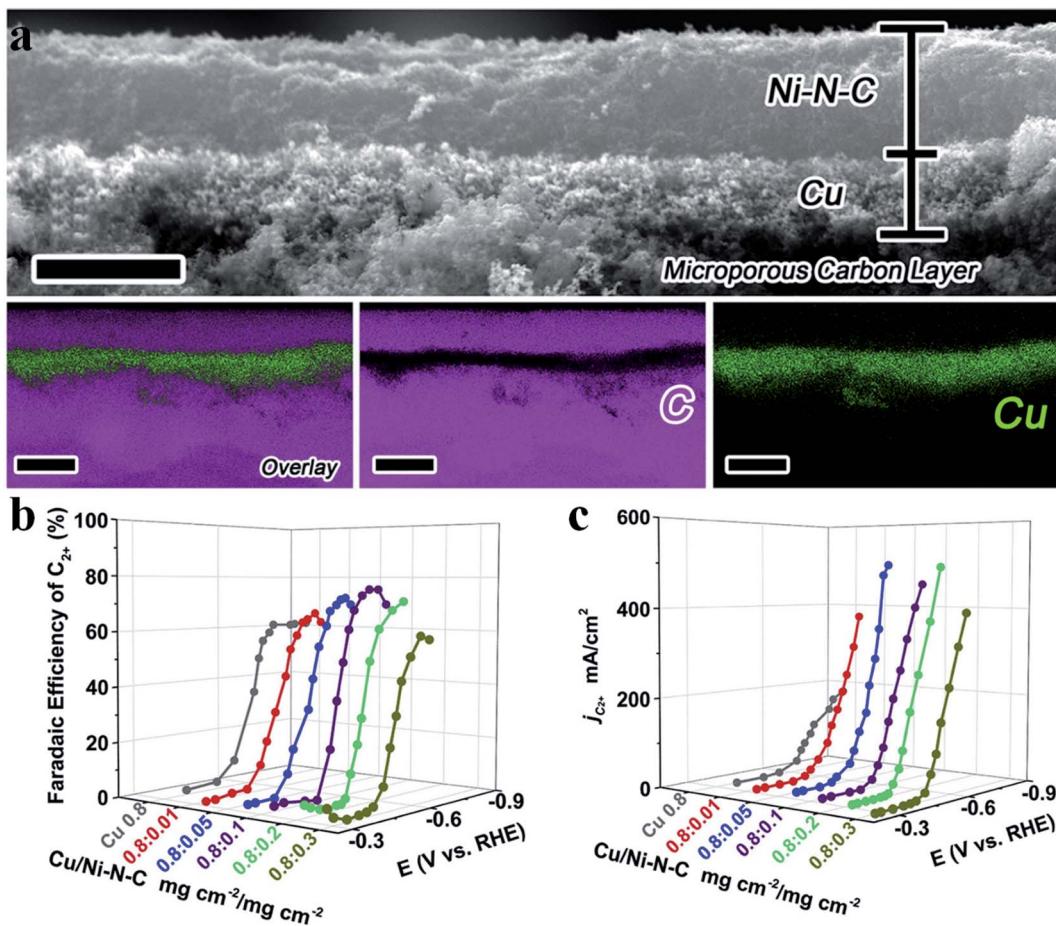


Fig. 13 (a) A cross-sectional SEM image and EDS elemental mapping of a Cu/Ni-N-C tandem electrode with two catalyst layers. Scale bars: 4  $\mu$ m for the SEM image and 5  $\mu$ m for the elemental mapping. (b) FE $_{C_2^+}$  for the Cu/Ni-N-C tandem electrode with Ni-N-C loading varying from 0.01 to 0.3  $\text{mg cm}^{-2}$ . (c) Partial current density of the Cu/Ni-N-C tandem electrode with Ni-N-C loading varying from 0.01 to 0.3  $\text{mg cm}^{-2}$ . Reproduced with permission from ref. 115. Copyright (2020) Elsevier.

nanoparticles, which enabled them to reduce  $\text{CO}_2$  to CO with a FE of 95.7% at  $-0.85$  V vs. RHE.<sup>119</sup> Sun *et al.* reported that Sn single atoms supported on oxygen-deficient CuO could reduce  $\text{CO}_2$  to ethylene with a FE of 48.5%, resulting from the lowered CO dimerization energy due to Sn doping.<sup>120</sup> The  $\text{CO}_2$ RR is

Table 1 Products beyond CO using SACs in the  $\text{CO}_2$ RR

| SACs                       | Structures                    | Products                            | Ref. |
|----------------------------|-------------------------------|-------------------------------------|------|
| $\text{Sn}^{\delta+}$      | $\text{SnN}_2\text{C}_2$      | $\text{HCOOH}$                      | 99   |
| Sb SA/NC                   | $\text{SbN}_4$                | $\text{HCOOH}$                      | 101  |
| NiSn-APC                   | $\text{N}_4\text{-Ni-Sn-N}_4$ | $\text{HCOOH}$                      | 100  |
| Mo-NG                      | $\text{MoN}_4$                | $\text{HCOOH}$                      | 102  |
| CoPc/CNT                   | $\text{CoN}_4$                | $\text{CH}_3\text{OH}$              | 103  |
| CuSA/TCNFs                 | $\text{CuN}_4$                | $\text{CH}_3\text{OH}$              | 105  |
| SA-Zn/MNC                  | $\text{ZnN}_4$                | $\text{CH}_4$                       | 106  |
| CoPc@Zn-N-C                | $\text{ZnN}_4$                | $\text{CH}_4$                       | 116  |
| $\text{Cu-CeO}_2$          | $\text{Cu-O}_3$               | $\text{CH}_4$                       | 107  |
| $\text{Cu}_{0.5}\text{NC}$ | $\text{CuN}_4$                | $\text{C}_2\text{H}_5\text{OH}$     | 108  |
| $\text{Cu/C-0.4}$          | $\text{CuO}_4$                | $\text{C}_2\text{H}_5\text{OH}$     | 109  |
| Cu-N-C-800(900)            | $\text{Cu-N}_2(\text{N}_4)$   | $\text{C}_2\text{H}_4\&\text{CH}_4$ | 111  |
| Cu-SA/NPC                  | $\text{CuN}_4$                | $\text{CH}_3\text{COCH}_3$          | 110  |

limited by the scaling relationship. Hybridizing d-orbitals of transition metals with p-orbitals of main group elements or metal carbides or nitrides offers a promising strategy to break the scaling relationship. Jung *et al.* inserted a series of single metal atoms into the surface defect sites of TiC, denoted as  $\text{M}@d\text{-TiC}$ ,<sup>49</sup> and Ir@d-TiC was found to display a very low overpotential of only  $-0.09$  V to reduce  $\text{CO}_2$  to produce  $\text{CH}_4$ . pDOS revealed that the lack of sigma-type bonding interaction between \*CO and single Ir atoms in Ir@d-TiC resulted in an appreciable decrease in the limiting potential. Inspired by these studies, substrates beyond carbon deserve more attention to be studied.

#### 4. Summary and outlook

To sum up, in this review, we introduced the theoretical considerations to guide the design of  $\text{CO}_2$ RR catalysts in terms of HER suppression, generation of  $\text{C}_1$  products and formation of  $\text{C}_2^+$  products, which were later supported by experiments (Table 1 summarizes the products beyond CO using SACs in the  $\text{CO}_2$ RR). Although much progress has been made in this field,

many challenges still remain. In the following we list the main issues and offer our solutions to address these obstacles.

(1) Most of the SACs are prepared at high temperatures ( $>800^{\circ}\text{C}$ ), which makes the synthesis uncontrollable.<sup>121–123</sup> As a result, the construction of SACs with a precise coordination environment is difficult to realize. Up to now, the coordination number is solely determined by EXAFS. However, EXAFS can only give the average structure<sup>124–126</sup> of SACs instead of the local structure. The high similarity of the M–C, M–N, and M–O bonds makes it hard to exactly figure out the coordination structure and the coordination number. Also, even if SACs possess the same coordination number, many possible models exist. For example, for the M-SAC with a coordination number of 3, the structure can be M–N<sub>3</sub>, M–N<sub>3</sub>–C, or M–N<sub>3</sub>–V. Moreover, these species can be located in plane or at the edges. The above uncertainty leads to the divergence in the effect of coordination number. Without a definite structure, it is impossible for DFT calculation to simulate the reaction mechanism.<sup>127–130</sup> Preparing SACs at low temperature or designing immobilized molecular catalysts is able to ensure a well-defined structure.<sup>131–135</sup> Additionally, more advanced characterization techniques are needed to be developed to better study the structure of SACs.<sup>136–139</sup>

(2) The structure of SAC does not always remain constant during the electrochemical reaction. For example, Cu single atoms could be transformed into Cu clusters during the CO<sub>2</sub>RR. Whether SACs undergo structural transitions and identification of the actual active site(s) in SACs are still the conundrums. *In situ* characterization provides a platform to monitor the structural evolution of SACs during the reaction.<sup>140–144</sup> Time-resolved *in situ* measurements should be developed to figure out the true active sites and obtain an overall picture of the reaction mechanism.

(3) Multiple protonation and electron transfer steps are involved in the CO<sub>2</sub>RR, making the reaction mechanism very complicated.<sup>145–148</sup> For the C<sub>2+</sub> products, lots of possible pathways for C–C coupling are proposed but cannot be confirmed by the current characterization techniques.<sup>149</sup> Also, the

distribution of C<sub>2+</sub> products is broad, and the selectivity is rather poor. Furthermore, it is still unclear whether protonation and electron transfer happen simultaneously (PCET mechanism).<sup>150–154</sup> Without a thorough understanding of the reaction mechanism, designing and searching for highly active and selective catalysts would be challenging. Constructing SACs with a well-defined structure and coupling *in situ* techniques together with the rapid developing computational methods are conducive to elucidating the underlying reaction mechanisms<sup>155,156</sup> (Fig. 14).

(4) Most of the SACs are in the form of powder, and show unsatisfactory performance in real devices.<sup>157–161</sup> Particularly, the solubility of CO<sub>2</sub> is low in aqueous solution (34 mM) and the CO<sub>2</sub> mass diffusion limitation dominates the CO<sub>2</sub>RR particularly at high current densities. Hybridizing SACs with a gas diffusion support or designing monolithic SAC electrodes has the potential to tackle this challenge. Moreover, flow cells and membrane electrode assembly cells have been developed rapidly, which assists in further improving CO<sub>2</sub>RR performance to meet the industry requirement.<sup>162–167</sup>

## Author contributions

J. Z., H. B. Y., and B. L. conceived the topic and structure of the article. All authors reviewed and contributed to this paper.

## Conflicts of interest

There are no conflicts to declare.

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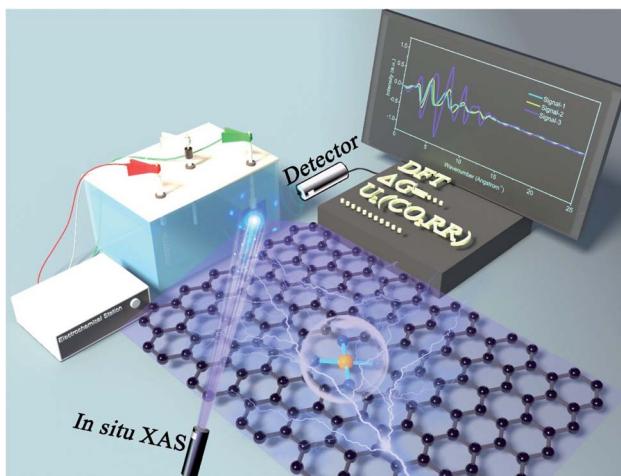


Fig. 14 *In situ* measurements and theoretical calculations prompt the development of SACs.



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