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## Harnessing single-atom catalysts for CO<sub>2</sub> electroreduction: a review of recent advances

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Electrochemical CO<sub>2</sub> reduction is an effective pathway to convert CO<sub>2</sub> into valuable fuels and chemicals, which provides a potential alternative to fossil fuel resources and plays a notable role in mitigating environmental issues and energy crises. The feasibility of the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) hinges on the development of catalysts that feature high activity, selectivity, and stability. As a new research frontier, single-atom catalysts (SACs) have shown immense potential in the field of CO<sub>2</sub> reduction by virtue of their unique geometric/electronic structures, and have also provided new opportunities for atomic-level understanding of structure–function relationships. Therefore, this review aims to outline recent advances of SACs for CO<sub>2</sub>RR. We start by introducing the current research status and general synthesis strategies of SACs, and then shift our focus to analyzing the various regulation strategies and deciphering the structure–function relationships of SACs in the CO<sub>2</sub>RR. Finally, we propose future directions and opportunities for CO<sub>2</sub>RR-oriented SACs, while also highlighting potential challenges that may be encountered along the way.

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### Broader context

Excessive emission of CO<sub>2</sub>, which causes environmental degradation and energy crises, has caused panic in the scientific community and the general population. Therefore, the development of effective CO<sub>2</sub> conversion and utilization technologies is urgent and of great significance. One promising approach is the use of clean energy to drive electrochemical CO<sub>2</sub> reduction, which can help mitigate the negative effects of CO<sub>2</sub> and generate high-value-added products. However, the extreme inertness of linear CO<sub>2</sub> molecules and the competing hydrogen evolution reaction severely affect their catalytic activity and selectivity. Fortunately, single-atom catalysts (SACs), with their unique geometric/electronic structures, have emerged as a frontier research area for the CO<sub>2</sub> reduction reaction (CO<sub>2</sub>RR) and have achieved significant progress. To accelerate the research progress of SACs in the CO<sub>2</sub>RR, it is necessary to summarize and review the current state of this field and provide guidance for future research. This article first introduces the basic parameters of the CO<sub>2</sub>RR and summarizes the mainstream reaction mechanisms for generating C<sub>1</sub> and C<sub>2</sub> products. Then, the current development status of SACs is outlined, along with common synthesis strategies. The application of SACs in the CO<sub>2</sub>RR is then highlighted, including analyzing the various regulation strategies and deciphering the structure–function relationships of SACs in the CO<sub>2</sub>RR. Finally, future potential directions and challenges confronted by SACs in the realm of the CO<sub>2</sub>RR are also contemplated.

## 1. Introduction

The continuous consumption of fossil fuels has led to excessive emission of CO<sub>2</sub> into the Earth's atmosphere, which has consequently caused climate change and environmental crises, and provoked great concern in the scientific community and the general population.<sup>1–5</sup> Besides, as CO<sub>2</sub> accounts for over 96% of the Martian atmosphere, utilizing CO<sub>2</sub> resources for Mars exploration is also a new research direction for future human space programs.<sup>6</sup> Thus, effective CO<sub>2</sub> conversion and utilization technologies are pressing and important grand research challenges in maintaining carbon neutrality balance and alleviating energy shortages. To address the CO<sub>2</sub> issue, different routes have been proposed: (1) capturing and storing

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During the past decades, a broad class of electrocatalysts has been developed for the CO<sub>2</sub>RR, including metals,<sup>28–31</sup> metal oxides,<sup>32–37</sup> metal alloys,<sup>38–41</sup> molecular compounds,<sup>42</sup> metal phosphides/chalcogenides,<sup>43,44</sup> and metal-free carbon-based materials.<sup>45–47</sup> Most notably, single-atom catalysts (SACs) have emerged as a new family of catalytic materials by virtue of their distinctive structural properties and exceptional catalytic performances.<sup>48,49</sup> As a new class of frontier materials, the SACs

feature maximized atomic utilization with their active sites isolated with each other but interacting with the support.<sup>50</sup> In 2011, Qiao *et al.* reported a single-atom platinum catalyst supported on iron oxide nanocrystallites (Pt<sub>1</sub>/FeO<sub>x</sub>), and the concept of a “single-atom” catalyst was proposed for the first time.<sup>51</sup> Since then, the concept was quickly accepted by the scientific community and the scope of relevant materials has broadened significantly. Various materials have been explored as the support (such as carbon materials,<sup>52,53</sup> MXenes,<sup>54</sup> oxides,<sup>55</sup> and carbides<sup>56</sup>), and the elements for the metal active centers have nearly covered all the non-radioactive metals in the periodic table.<sup>57,58</sup> The CO<sub>2</sub>RR over SACs can be traced back to the 1970s, when molecular catalysts (cobalt/nickel phthalocyanines) were used as the active sites.<sup>59</sup> With the development of synthesis technology, characterization technology (high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM) and X-ray absorption spectroscopy (XAS), in particular), and theoretical computational chemistry, the establishment of the structure–function relationship between the structure of SACs and the performance of the CO<sub>2</sub>RR has made great progress. Specifically, SACs have adjustable coordination environments and structures, making it easier to obtain uniform catalytic active centers. Furthermore, SACs can also serve as an ideal bridge between homogeneous and heterogeneous catalysis.<sup>48–50</sup> For the CO<sub>2</sub>RR, the reaction process typically involves multiple PCET steps accompanied by complex intermediates, and SACs with well-defined structures have become an ideal research model. This could help to identify the reaction mechanism and to understand the structure–function relationship of SACs in the CO<sub>2</sub>RR, guiding us to develop new advanced electrocatalysts. For example, SACs featuring Ag, Mn, Fe, and Ni single-atom active sites often exhibit excellent CO selectivities.<sup>27</sup> In the process of the rational design of CO<sub>2</sub>RR catalysts, researchers have found that the generation of non-CO products (such as C<sub>2+</sub> products) is very difficult and complex.<sup>60</sup> Because of the isolation and simplicity of their active sites, SACs are not so competent in some cases, prompting researchers to develop dual-atom catalysts or multi-atom catalysts (DACs or MACs) with more than one type of active sites.<sup>61,62</sup> There could be a synergistic effect between the dual-atom sites or multi-atom sites, providing more possibilities and pathways for the generation of high value-added products.<sup>63–67</sup>

Compared with other types of heterogeneous catalysts, SACs have unique advantages in geometric/electronic structures, which gives them great potential to become marvellous catalysts for the CO<sub>2</sub>RR. In this review, as shown in Fig. 1, we use the metaphor of an alchemical furnace as the main concept, with three supporting pillars representing the general synthesis strategies for SACs. The four different “elixirs” within the furnace chamber represent the diverse regulation strategies for SACs in CO<sub>2</sub>RR applications. Eventually, the reactant CO<sub>2</sub> undergoes transformations within this alchemical furnace to produce various products. At the end of this review, we present an outlook on the future directions, opportunities, and challenges in the field of SACs for the CO<sub>2</sub>RR.

Half-cell reaction	Standard potentials
$2\text{H}^+ + 2\text{e}^- \rightarrow \text{H}_2$	-0.42
$\text{CO}_2 + \text{e}^- \rightarrow \text{*CO}_2^-$	-1.9
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$	-0.52
$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$	-0.61
$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$	-0.51
$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$	-0.38
$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$	-0.24
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_4 + 4\text{H}_2\text{O}$	-0.34
$2\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$	-0.33

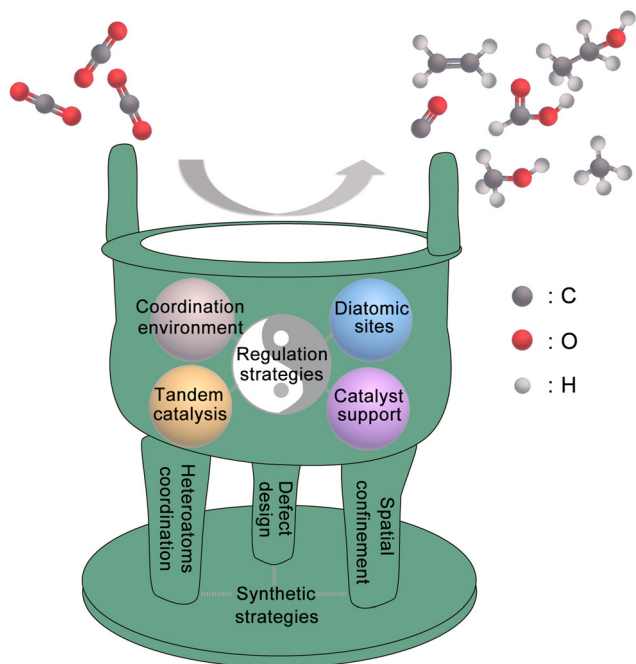


Fig. 1 Schematic diagram of the SACs for the CO<sub>2</sub>RR in this review (including the general synthesis strategies for SACs and the regulation strategies of SACs for the CO<sub>2</sub>RR).

## 2. Fundamental parameters and reaction mechanisms of the CO<sub>2</sub>RR

### 2.1 Fundamental parameters of the CO<sub>2</sub>RR

It is necessary to introduce the fundamental parameters before proceeding further with this review. At present, the standard metrics used to evaluate and compare the performance of CO<sub>2</sub>RR electrocatalytic materials mainly include the following: faradaic efficiency (FE), onset potential, current density, partial current density, stability, turnover frequency (TOF).<sup>25,68</sup>

**2.1.1 Faradaic efficiency.** FE refers to the percentage of the number of electrons consumed in the generation of the target product to the total number of electrons consumed, which can be calculated using the following formula:  $FE = \alpha nF/Q$ . Among them,  $\alpha$  is the number of electron transfers that generate a specific product (for example, if CO<sub>2</sub> is reduced to carbon monoxide (CO), the number of electrons transferred in this process is 2,  $\alpha = 2$ );  $n$  is the total amount of a specific product (in moles);  $F$  is the Faraday constant (96 485 C mol<sup>-1</sup>);  $Q$  represents the total amount of charge during the CO<sub>2</sub>RR process. By analysing the FE, the difference in selectivity of different catalysts for the CO<sub>2</sub>RR can be directly compared.

**2.1.2 Onset potential.** Thermodynamically, CO<sub>2</sub>RR is a non-spontaneous process. The onset potential is the lowest externally applied potential that can initiate the CO<sub>2</sub>RR (with the generated target product detectable). Since there is a certain potential barrier to overcome in the process of the CO<sub>2</sub>RR, the onset potential is generally more negative than the standard reduction potential. Overpotential is the difference between the thermodynamic standard potential and the external potential

of a specific CO<sub>2</sub>RR, typically used to activate inert CO<sub>2</sub> molecules to form \*CO<sub>2</sub><sup>-</sup> anionic radicals, driving material exchange and electron transfer in the CO<sub>2</sub>RR process. The onset potential is the parameter that can directly indicate the magnitude of the overpotential and assess the catalytic activity of the electrocatalyst.

**2.1.3 Current density.** Current density refers to the current passing through a unit electrode area, which is the ratio of the current magnitude to the electrochemical active area, and can be used to estimate the reaction rate. The magnitude of current density is one of the indicators of whether a catalytic system can be commercialized.

**2.1.4 Partial current density.** Partial current density expresses the effective current density that drives the formation of a specific product, which can be obtained by multiplying the FE for that specific product by the total current density. Commonly, the partial current density is not only dependent on the activity of the electrocatalyst itself, but also influenced by experimental conditions (electrodes, cell components, electrolyte, etc.). For example, the H-type cell configuration is limited by the solubility and diffusion of CO<sub>2</sub> in the aqueous electrolyte, whereas the flow cell configuration is equipped with gas diffusion electrode components (which can continuously provide CO<sub>2</sub> gas and electrolyte), thus achieving high current density.<sup>69</sup>

**2.1.5 Stability.** Stability is an important metric that indicates whether a catalyst can be commercially applied. Therefore, stability is no less important for a catalyst than its activity and selectivity. At present, the stability tests of catalysts in the laboratory usually take only a few dozen hours, which is far from enough for the commercialization of catalysts. The decline of stability is usually caused by the coupling of the deactivation of the catalytic active site, the destruction of the catalyst structure, and the continuous consumption of electrolytes. An ideal CO<sub>2</sub>RR catalyst should be designed to retain both current density and FE without increasing the overpotential during long-term continuous operation.

**2.1.6 Turnover frequency.** For decades, TOF has been an accurate descriptor for the intrinsic activity of catalysts. While current density is important in determining the apparent activity, but it is affected by parasitic reactions centered on the catalyst and competitive reactions centered on the electrolyte. Fortunately, TOF provides a precise measure of the intrinsic activity without involving these electrocatalytic phenomena. TOF refers to the quantity of target products produced on one active site in unit time, and its calculation formula is as follows:  $TOF = [\text{product (mol)}]/[\text{active sites (mol)}]/\text{time}$ . Among these, there are multiple analytical methods available to quantify reactants or products; however, determining the exact number of active sites is often the most challenging task. In particular, for cluster/nanoparticle catalysts, even when the active sites are identified, each site may have a different chemical environment. In contrast, for SACs, the situation is much simpler. Currently, it is presumed that the active sites in SACs are isolated, and their chemical environments are almost uniform. Hence, it can be assumed that each individual metal atom acts as an active site.<sup>25</sup>



**2.2.1 Pathways for C<sub>1</sub> products.** CO is the most common product of the CO<sub>2</sub>RR, and a large portion of SACs (such as Fe, Co, Ni, and Mn) exhibit high CO selectivity (Fig. 2).<sup>70</sup> Although researchers have made significant efforts to analyze the pathways of CO generation, a clear picture of the reaction mechanism remains controversial. At present, the reaction pathway from CO<sub>2</sub> to CO through \*COOH intermediates is widely acknowledged, which can be achieved through a PCET process or proton transfer process after a preferential electron transfer process (Fig. 3).<sup>70–74</sup> The resulting \*COOH intermediate would undergo the next PCET process to convert into \*CO, and the weakly bound \*CO would eventually desorb from the catalyst surface to produce CO. In the generation process of other C<sub>1</sub> products (such as HCHO, CH<sub>3</sub>OH, and CH<sub>4</sub>), \*CO is widely

Unlike other C<sub>1</sub> products, the generation of HCOOH or HCOO<sup>−</sup> has a reaction pathway of its own. The generation of HCOOH or HCOO<sup>−</sup> may be achieved through an intermediate, which is believed to be mainly through the binding of oxygen atoms to the catalyst surface, and the generation of this intermediate may have two different pathways: (1) CO<sub>2</sub><sup>−</sup> radicals bind to the catalyst surface and react with adjacent water molecules or protons to generate HCOO<sup>−</sup> or HCOOH; (2) CO<sub>2</sub> is directly inserted into metal-hydrogen or metal-hydroxyl bonds to form intermediates, which further yields HCOOH or HCOO<sup>−</sup>.<sup>70,77</sup>

**2.2.2 Pathways for C<sub>2</sub> products.** The reaction mechanisms of C<sub>2</sub> products are even more complex. Here we summarize the plausible reaction mechanisms of the two main C<sub>2</sub> products: C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH (Fig. 3). \*CO is considered a key intermediate for the formation of C<sub>2</sub> products. It can directly form the \*C<sub>2</sub>HO<sub>2</sub> intermediate through symmetric dimerization followed by further hydrogenation. Alternatively, it can first undergo hydrogenation to produce \*CHO or \*COH, which then asymmetrically couple with \*CO to yield the \*C<sub>2</sub>HO<sub>2</sub> intermediate.<sup>13,71,78</sup> Among the various catalysts developed so far, Cu-based catalysts are the only ones widely recognized capable of catalyzing the CO<sub>2</sub>RR to C<sub>2+</sub> products because of their moderate binding energy with \*CO.<sup>79,80</sup> After the C–C coupling, multiple PCET steps ensue to obtain the key \*C<sub>2</sub>H<sub>3</sub>O intermediate that determines the formation of C<sub>2</sub>H<sub>4</sub> and C<sub>2</sub>H<sub>5</sub>OH products. However, in most catalyst systems, the selectivity for C<sub>2</sub>H<sub>4</sub> is higher than that for C<sub>2</sub>H<sub>5</sub>OH because the energy barrier from the \*C<sub>2</sub>H<sub>3</sub>O intermediate to the C<sub>2</sub>H<sub>4</sub> product is lower than to the C<sub>2</sub>H<sub>5</sub>OH product.<sup>81</sup> Although Cu is considered to have unique advantages in the selectivity of C<sub>2+</sub> products, there are few reports on Cu SACs for producing C<sub>2+</sub> products, as it is difficult to promote C–C coupling or \*CO dimerization on isolated Cu single atoms. Thus, in the future, more modifications on Cu-based catalysts will be considered to construct more homonuclear or heteronuclear active sites, in order to expand the range of C<sub>2+</sub> products and to improve their selectivity.<sup>82–84</sup>

### 3.1 Synthesis strategies of SACs

The term “SACs” was coined on the basis of the characteristics of their active centers; however, in reality, individual atoms





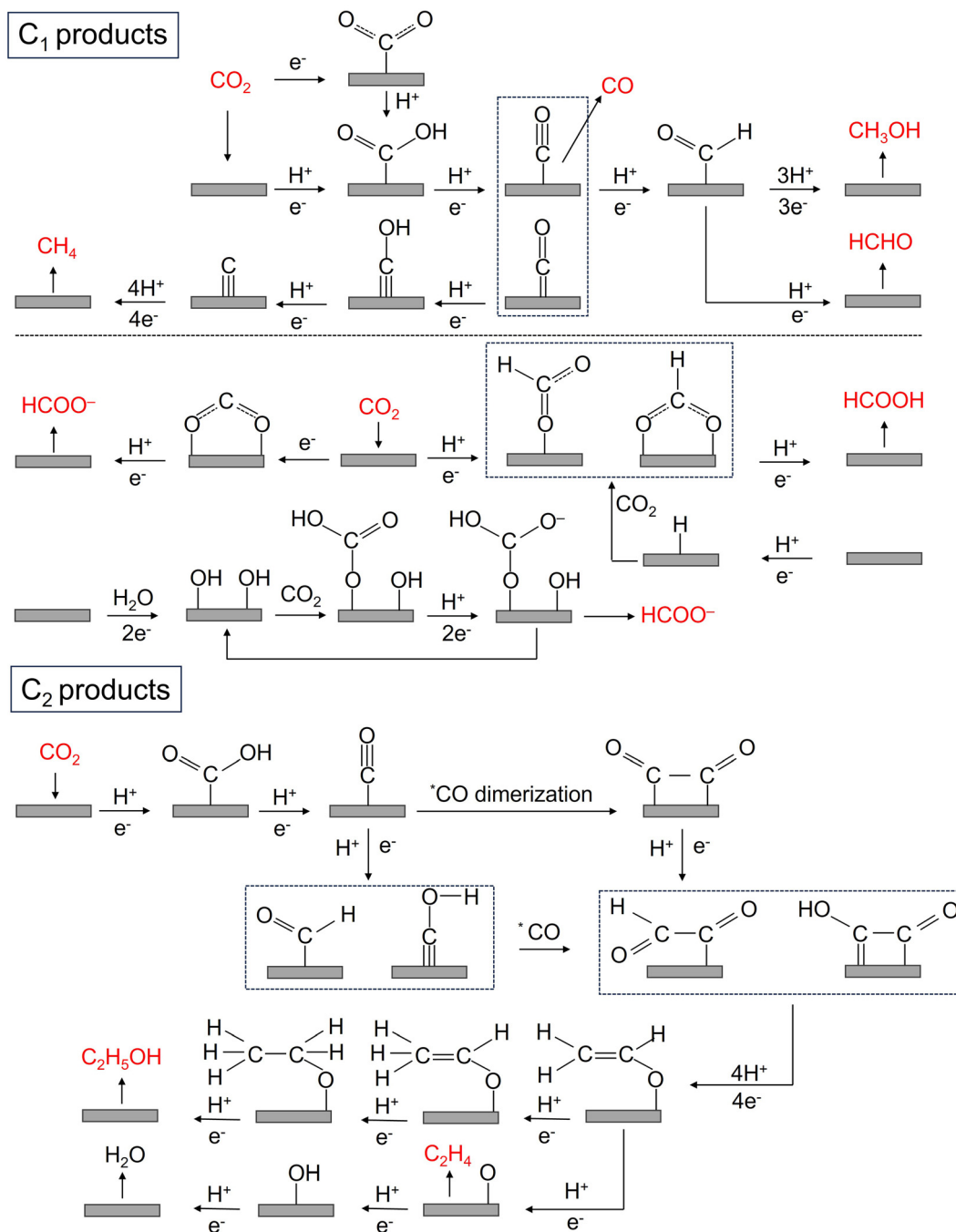


Fig. 3 The possible reaction pathways of C<sub>1</sub> and C<sub>2</sub> products in the CO<sub>2</sub>RR.

cannot exist in isolation but instead rely on a supporting material.<sup>48,49</sup> Owing to their high surface energy, isolated metal atoms have a tendency to aggregate into thermodynamically more stable metal clusters. Hence, the interaction between the support and single atoms is crucial in preventing the aggregation of individual atoms. Since the concept of “single-atom-catalysts” emerged in 2011,<sup>51</sup> various strategies have been proposed to synthesize SACs with high metal loadings and high CO<sub>2</sub>RR performances. In this section, we mainly discuss the challenges and current strategies for increasing the metal

loading and tuning the electronic structure of SACs, which are categorized into “heteroatom coordination strategy”, “spatial confinement strategy” and “defect design strategy”. In addition, some other advanced synthesis strategies of SACs are also introduced.

**3.1.1 Heteroatom coordination strategy.** The rational design of coordination sites with the aim of adsorbing and binding metal precursors or metal atoms to prevent their agglomeration and migration has been a basic design principle for the synthesis of SACs. Owing to the strong interaction



between metal atoms and coordinating atoms, metal single atoms can be uniformly and firmly anchored onto the supports. The construction of highly active and stable SACs using the coordination strategy requires the selection of suitable reactants (*e.g.*, metal precursors and coordination polymorphs) and appropriate experimental conditions. Several non-metallic elements with lone pairs of electrons are good coordination sites because of their affinity for metals, such as N, O and S.<sup>20,21,48,85</sup>

Many studies have already shown that the physicochemical state of SACs can be optimized by adjusting the coordination

number, coordination structure and coordination environment of the metal single-atom centers, thus further improving their CO<sub>2</sub>RR performance. The coordination number of the central metal atoms can modulate the electronic structure of the catalyst and thus alter the catalytic performance. Wang *et al.* reported two Co-based catalysts with different coordination numbers, denoted as Co-N<sub>4</sub> and Co-N<sub>2</sub>. The catalysts were prepared by adjusting the pyrolysis temperature to control the extent of volatilization (Fig. 4a).<sup>86</sup> Zhang *et al.* devised a post-synthetic metal substitution (PSMS) strategy in combination

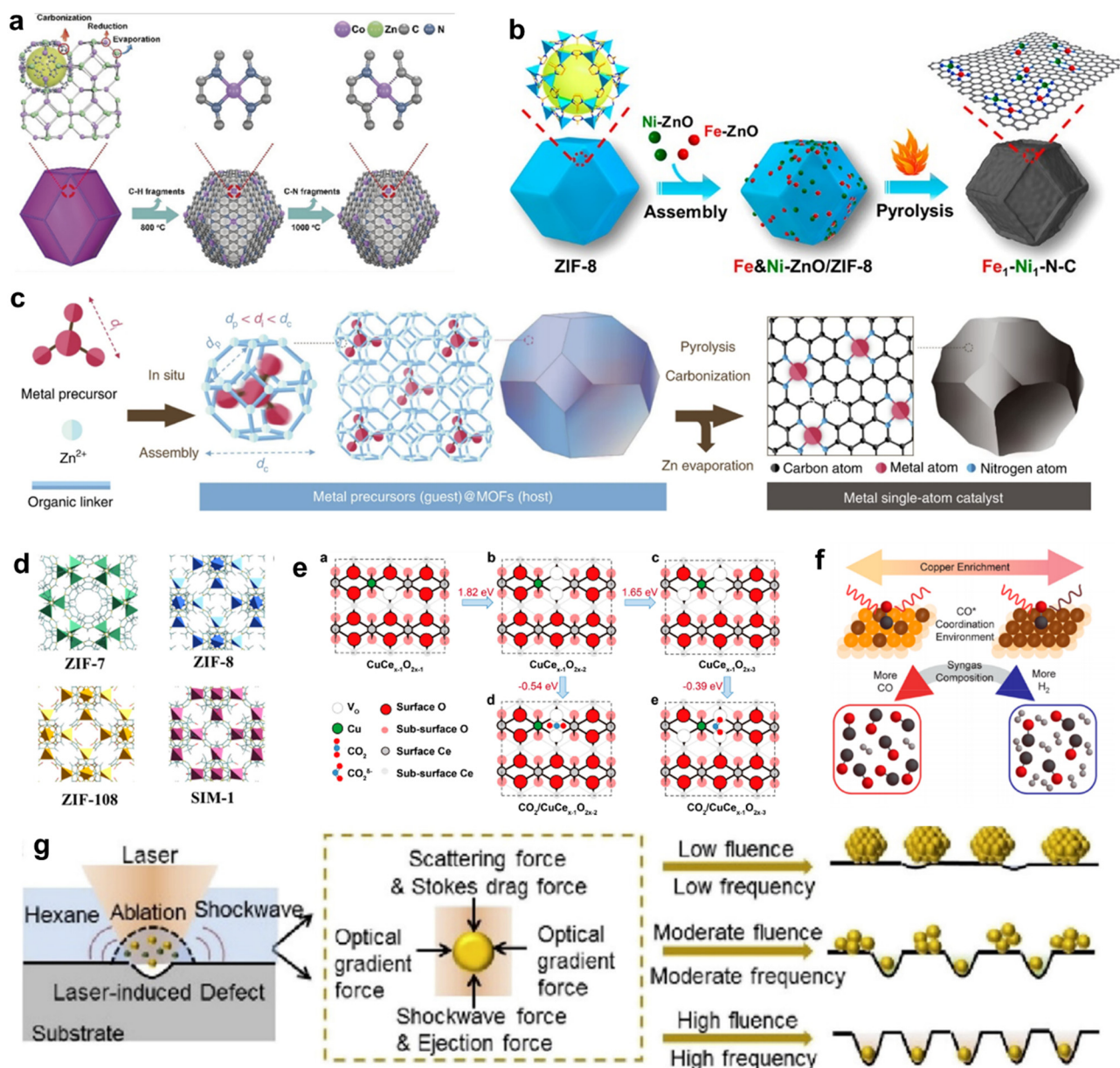


Fig. 4 (a) The formation process of Co-N<sub>4</sub> and Co-N<sub>2</sub>.<sup>86</sup> (b) Schematic illustration for the construction of Fe<sub>1</sub>-Ni<sub>1</sub>-N-C with neighbouring Fe and Ni single-atoms based on ZIF-8.<sup>89</sup> (c) Scheme of the host-guest strategy for the fabrication of isolated metal single-atom-site catalysts.<sup>100</sup> (d) The model structures of ZIF catalysts.<sup>102</sup> (e) Theoretical calculations of the most stable structures of Cu-doped CeO<sub>2</sub>(110) and their effects on CO<sub>2</sub> activation.<sup>106</sup> (f) Scheme depicting the relationship between the Cu-enriched Au surface, *in situ* characterization of CO\* coordination, and syngas composition.<sup>113</sup> (g) Schematic diagram depicting the synthesis of Pt nanoparticles, Pt clusters, and Pt single atoms under laser planting with low, moderate, and high fluences and frequencies, respectively.<sup>118</sup>



**3.1.2 Spatial confinement strategy.** Spatial confinement has been developed as an effective strategy for constructing SACs with precisely defined microenvironments. The best carriers for encapsulation are porous materials such as zeolites, COF, MOFs/zeolite imidazolium salt frameworks (ZIFs), and porous carbon matrices (PCM).<sup>96–99</sup> Li *et al.* developed a general host-guest strategy for preparing various metal SACs on nitrogen-doped carbon (M/CN, M = Pt, Ir, Pd, Ru, Mo, Ga, Cu, Ni, Mn) (Fig. 4c).<sup>100</sup> The activity of Ir<sub>1</sub>/CN is 16 times and 19 times that of Pd/C and Pt/C, respectively. In addition, Ir<sub>1</sub>/CN showed high tolerance to CO poisoning. Zhao *et al.* prepared a catalyst containing single Ni sites using MOFs for efficient electrocatalytic reduction of CO<sub>2</sub>.<sup>101</sup> This synthesis is based on ion exchange between Zn nodes and Ni ions adsorbed in the MOF cavity. Jiang *et al.* studied ZIF-8, ZIF-108, ZIF-7, and SIM-1 with the same SOD (sodium salt) topology and different CO<sub>2</sub>RR organic ligands in an aqueous solution (Fig. 4d).<sup>102</sup> *In situ* XAS measurements and density functional theory (DFT) calculations

**3.1.3 Defect design strategy.** Isolated single metal atoms can be stably anchored on supports through the design of surface defects, which have been developed as an effective method for synthesizing SACs. Various vacancies and coordination-unsaturated sites are often used not only to trap and stabilize metal single atoms, but also to alter the surrounding



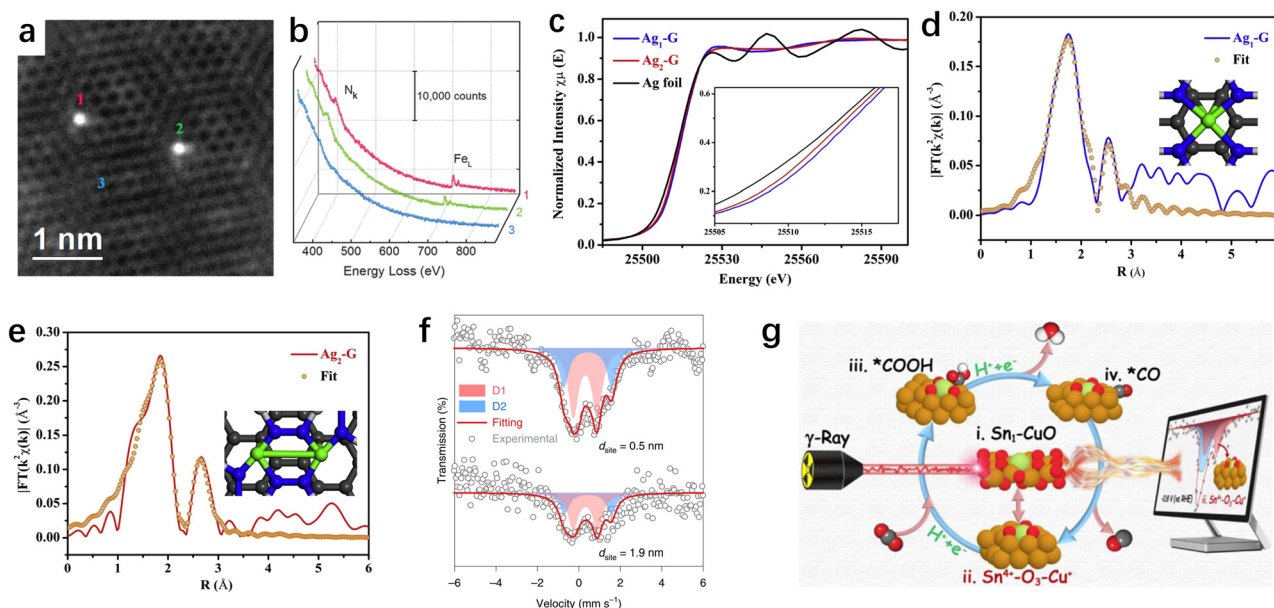
**3.1.4 Other strategies.** Other than the strategies discussed above, there have been several more novel synthesis strategies

In addition to the above-mentioned synthesis methods, a few other special strategies have been proposed including nanoparticles becoming single atoms *via* solid diffusion,<sup>119–121</sup> solid-state atom diffusion,<sup>122,123</sup> *in situ* thermal atomization methods,<sup>119</sup> electrospinning polymer nanofibers,<sup>124</sup> and cross-linking and self-assembly of graphene quantum dots.<sup>125</sup>

Upon providing an overview of the synthesis strategies for SACs, determining the geometric structure and electronic environment of SACs is crucial for investigating their structure–function relationship in CO<sub>2</sub>RR applications. Primarily, ascertaining the



**3.2.2 XAS.** AC-HAADF-STEM is capable of visualizing single metal atoms loaded on solid supports, particularly carbon supports, by utilizing their different  $Z$  contrasts. However, it does not provide information regarding the electronic states and coordination configurations of the metal active sites. In contrast, XAS (including X-ray absorption near edge structure (XANES) and extended X-ray absorption fine structure (EXAFS)) is a powerful technique for characterizing the electronic states, coordination and geometric structures of metal active sites.<sup>64</sup> XANES is sensitive in capturing information related to average valence states and electron configurations. The near-edge position in XANES corresponds to the oxidation state of the target element, where higher oxidation states require greater energy to excite core electrons. On the other hand, EXAFS provides crucial details about the local geometry and coordination

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environment of the single atomic sites. By fitting the results from EXAFS, important parameters such as bond length and coordination numbers can be inferred. Additionally, the bonding and coordination configuration of the metal centers can also be reasonably deduced through the analysis of EXAFS data. We previously reported a method for customizing metal active sites, wherein we pre-synthesized mononuclear and binuclear Ag complexes as metal precursors. These precursors were then dispersed on graphene (G) to successfully synthesize Ag1-G and Ag2-G catalysts.<sup>127</sup> Combining the customized synthesis strategy with XAS results, and conducting a detailed analysis of other test results along with fitting of EXAFS data, we have confirmed that the coordination configurations of the active centers in Ag1-G and Ag2-G catalysts are Ag-N<sub>4</sub> and AgN<sub>3</sub>-AgN<sub>3</sub> structures, respectively (Fig. 5c-e).

**3.2.3 Mössbauer spectroscopy.** Mössbauer spectroscopy is an effective technique used to probe the coordination structures and spin states of various Mössbauer-active metal centers (such as Fe, Sn, Sb, *etc.*) in SACs.<sup>128</sup> Under ambient temperature testing conditions, normally the nuclear transitions of <sup>57</sup>Fe and <sup>119</sup>Sn have a higher probability of exhibiting the Mössbauer effect. Currently, research utilizing Mössbauer spectroscopy to investigate the electronic states of SACs is predominantly focused on the elements Fe and Sn. Jin *et al.* conducted a study where they designed Fe-N<sub>4</sub> catalysts with varying densities of single-atom active sites, aiming to investigate the influence of inter-site distances on the properties of Fe-N<sub>4</sub>.<sup>129</sup> Through Mössbauer spectroscopy testing, the results demonstrated that at inter-site distances of 0.5 and 1.9 nm in Fe-N<sub>4</sub>, the deconvoluted transmission profiles provided evidence that D1 and D2 doublets dominate most Fe species for the two samples (Fig. 5f). Notably, D1 was assigned to the low-spin Fe(II)-N<sub>4</sub> species acting as a highly active catalytic site, whereas D2 was associated with a medium-spin Fe(II)-N<sub>4</sub> species. Chen *et al.* reported a copper oxide-supported atomically dispersed Sn catalyst for the CO<sub>2</sub>RR.<sup>130</sup> In their study, they employed <sup>119</sup>Sn Mössbauer spectroscopy as a probe technique to track the catalyst's metastable species. The Mössbauer spectroscopy results revealed that the atomically dispersed Sn<sup>4+</sup> sites on the CuO substrate underwent a transformation from Sn<sup>4+</sup>-O<sub>4</sub>-Cu<sup>2+</sup> to a metastable state of Sn<sup>4+</sup>-O<sub>3</sub>-Cu<sup>+</sup> during the CO<sub>2</sub>RR (Fig. 5g)

## 4. Structure–function relationship of SACs in electrochemical CO<sub>2</sub>RRs

### 4.1 Coordination environment regulation

The coordination environment of SACs can directly influence the electronic and geometric structure of the metal active site, thereby altering the adsorption/desorption processes of key intermediates in the CO<sub>2</sub>RR. Additionally, different coordination environments can result in distinct microenvironments for the CO<sub>2</sub>RR, such as interfacial water and local pH, playing a significant regulatory role in the reaction process. In this section, we primarily focus on the discussion of two types

of coordination regulations: in-plane and out-of-plane coordination.

**4.1.1 In-plane coordination.** Regulation of the in-plane coordination environment typically involves the control of atoms in the first shell of the metal active site, which allows for a direct modification of the oxidation state or electronic structure of the metal centers.<sup>131</sup> As is well known, Fe SACs with FeN<sub>4</sub> sites exhibit a lower CO<sub>2</sub>RR reduction onset potential and can efficiently electrochemically reduce CO<sub>2</sub> to CO at low potentials. However, this high activity and selectivity rapidly decrease as the potential increases, and high CO selectivity can only be achieved within a narrow voltage range. The main reason for this is the adsorption equilibrium issue of \*COOH and \*CO key intermediates on Fe SACs (with a higher formation energy barrier for \*COOH and stronger adsorption of \*CO). To this end, Zhao *et al.* replaced N with O atoms and synthesized Fe SACs with a unique FeN<sub>2</sub>O<sub>2</sub> coordination structure using a strategy of thermal decomposition of oxygen-containing MOF precursors (Fig. 6a).<sup>132</sup> Compared to N, O atoms have higher electronegativity and show tremendous potential in regulating the reaction kinetics. The synthesized FeN<sub>2</sub>O<sub>2</sub> catalyst showed over 95% selectivity within the voltage range of -0.4 to -0.8 V. Theoretical calculations indicated that, with O coordination, the Fe sites exhibited a lower formation energy for \*COOH and facilitated \*CO desorption. Recently, Zhang *et al.* reported for the first time the Ga-N<sub>3</sub>S-PC SASC with a flexible structural feature achieved through coordination with S and P.<sup>133</sup> This unique structure enables the Ga active sites to exhibit excellent CO<sub>2</sub>RR performance with a selectivity of over 90% towards CO. Theoretical simulations suggest that the Ga-N<sub>3</sub>S-PC sites can undergo structural transformations and oscillations during the reaction process, optimizing the adsorption energy of \*COOH to adapt to the CO<sub>2</sub>RR process. Compared to the Ga-N<sub>4</sub> structure, Ga-N<sub>3</sub>S-PC exhibits higher activity and stability.

H<sub>2</sub>O is a molecule that directly participates in the reaction, generating H through dissociation for the PCET process. Therefore, it is crucial to regulate the interfacial water for efficient CO<sub>2</sub>RR.<sup>134</sup> In this regard, besides directly adjusting the electronic structure of the metal center by optimizing the first coordination sphere, controlling the interfacial microenvironment through non-coordinating heteroatom doping also has significant importance in the development of high-performance SACs. For example, in order to promote the synergistic adsorption and activation of CO<sub>2</sub> and H<sub>2</sub>O, Liu *et al.* constructed a SASC with FeN<sub>4</sub>/graphitic N atomic interface sites through a H<sub>2</sub>-assisted pyrolysis strategy, which achieved a CO faradaic efficiency of over 90% within the range of -0.3 to -0.8 V.<sup>135</sup> *Operando* attenuated total reflection surface enhanced infrared absorption spectroscopy (ATR-SEIRAS) and the first-principle calculations indicate that the presence of graphitic N sites facilitates the co-adsorption of H<sub>2</sub>O, thereby promoting the activation of CO<sub>2</sub> and its conversion into the key intermediate \*COOH (Fig. 6b). In another work, Sun *et al.* achieved efficient electrochemical CO<sub>2</sub> to CO conversion on Mo SACs through the incorporation of Se into the carbon support.<sup>136</sup> The study





**Fig. 6** (a) Schematic illustration of the preparation of  $\text{Fe}_3\text{N}_2\text{O}_2/\text{NC}$ .<sup>132</sup> (b) Synthesis method and  $\text{CO}_2\text{RR}$  performance of  $\text{H}_2\text{-FeN}_4/\text{C}$ .<sup>135</sup> (c) Schematic diagram of the reaction mechanism of  $\text{MoSA-SeSA}$ .<sup>136</sup> (d) Schematic of the synthetic process for well-designed iron single-atomic catalysts.<sup>138</sup> (e)  $\text{CO}_2\text{RR}$  pathways on Fe sites of different catalyst configurations.<sup>138</sup> (f) Schematic of the single-atom nanozyme  $\text{Ni-N}_5\text{-C}$ .<sup>140</sup> (g) Orbital interactions between Ni centers ( $d_{z^2}$ ,  $d_{xz/yz}$ ) and adsorbed  $\text{COOH}$  on  $\text{Ni-N}_4\text{-C}$  and  $\text{Ni-N}_5\text{-C}$ .<sup>140</sup>

demonstrates that the introduction of neighbouring Se (6.0 Å) can effectively improve the reaction thermodynamics of the

$\text{MoN}_4$  sites through long-range electronic interactions, promoting  $^*\text{CO}$  desorption. On the other hand, the remaining Se far







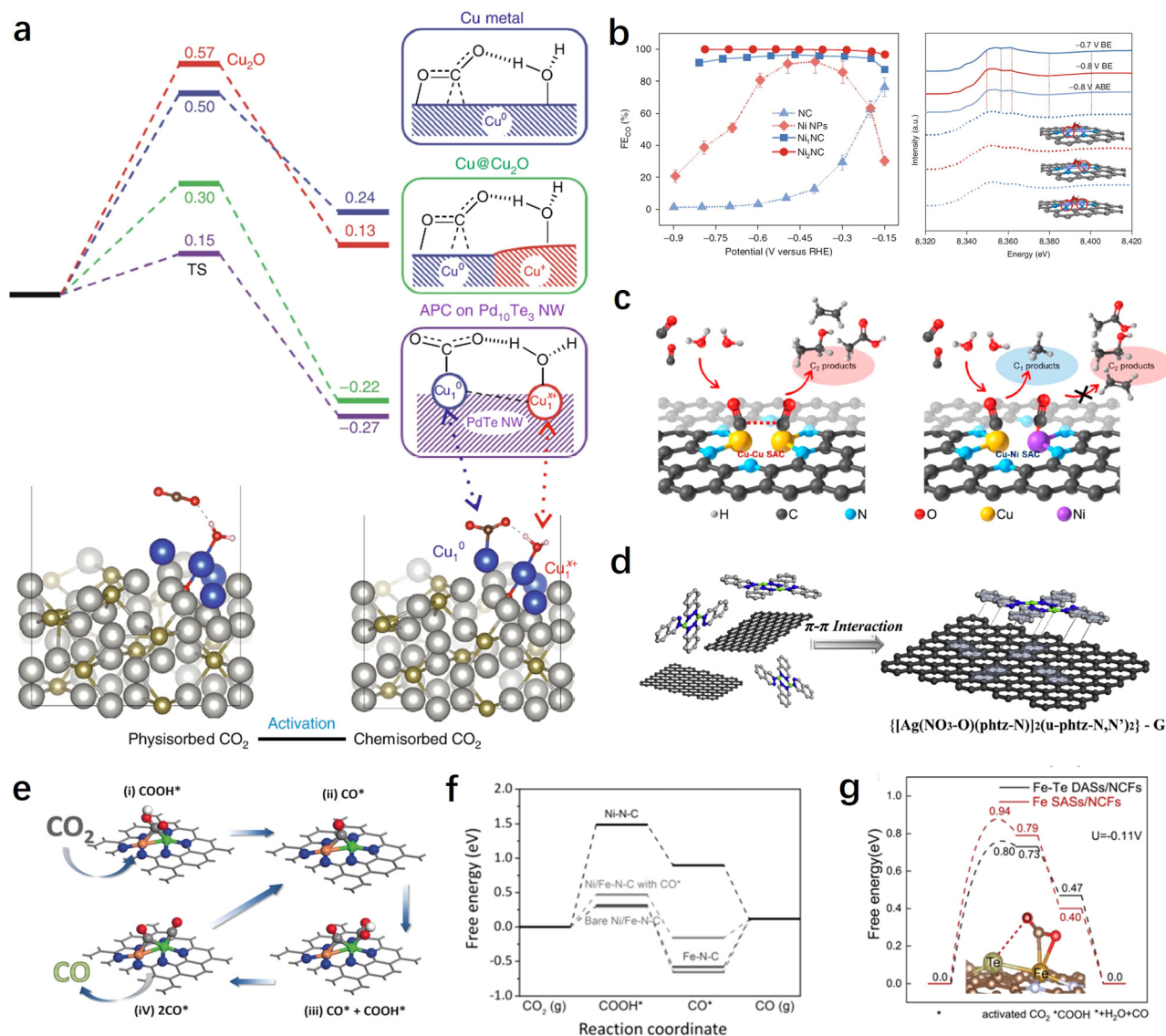


Fig. 7 (a) Free energy profiles for the CO<sub>2</sub> activation mode of Cu-APC catalysts.<sup>111</sup> (b) CO<sub>2</sub>RR performance and XANES spectra of Ni<sub>2</sub>NC catalysts.<sup>96</sup> (c) Schemes showing the structures and products for the CO<sub>2</sub>RR on dual Cu-Cu and Cu-Ni SACs.<sup>146</sup> (d) Schematic illustration of the synthesis process of Ag<sub>2</sub>-G catalysts.<sup>127</sup> (e) The catalytic mechanism on diatomic NiFe catalysts based on the optimized structures of adsorbed intermediates COOH\* and CO\*.<sup>147</sup> (f) Calculated free energy diagrams for the CO<sub>2</sub>RR yielding CO on different catalysts.<sup>147</sup> (g) The free energy diagram of the CO<sub>2</sub>RR on Fe-Te DASs/NCs.<sup>149</sup>

Despite some breakthroughs in the activity and selectivity of DACs for the CO<sub>2</sub>RR, there are still difficulties and challenges in the precise synthesis and controllable preparation of dual-atomic sites. To this end, Li *et al.* have developed a dual-core metal molecular pre-synthesis and post-adsorption strategy.<sup>127</sup> They first synthesized a well-defined binuclear Ag complex and then obtained DACs with AgN<sub>3</sub>-AgN<sub>3</sub> sites through the π-π interaction between the complex and graphene, as well as low-temperature treatment (Fig. 7d). These AgN<sub>3</sub>-AgN<sub>3</sub> sites demonstrated greater advantages in synergistic adsorption and activation of CO<sub>2</sub> compared to single Ag sites.

**4.2.2 Heteronuclear diatomic sites.** The synergistic effect of bimetallic interactions occurs not only between two identical metal atoms but also between two different metal atoms.

The coordination of d orbitals between heteronuclear metals allows for flexible modulation of the active center, reducing energy barriers, and thereby generating unexpected catalytic performance. For example, the rate-determining steps for the CO<sub>2</sub>RR on Ni-NC and Fe-NC are CO<sub>2</sub>(g) → \*COOH and \*CO → CO(g), respectively, due to the weak adsorption of \*COOH on Ni-NC and strong adsorption of \*CO on Fe-NC. This naturally leads to a reasonable conjecture and consideration: can their advantages in the reaction be maximized by combining them to achieve an optimal performance? Based on this, Ren *et al.* ingeniously designed an isolated bimetallic Ni-Fe site.<sup>147</sup> Studies have shown that during the CO<sub>2</sub>RR process, the bimetallic Ni-Fe center undergoes structural evolution to a CO-adsorbed moiety, which greatly reduces the formation energy

### 4.3 Tandem catalytic regulation

Potential matching determines the compatibility of different components, while spatial distribution determines the efficiency of the tandem reaction.<sup>156</sup> The generated CO on SACs often needs to spill over to adjacent Cu sites, and if the distance between them is too far, the tandem process will be hindered.



Fig. 8 (a) Schematic diagrams of the tandem systems of Cu/Ni-NAC hybrid catalysts.<sup>154</sup> (b) Faradaic efficiency of C<sub>2</sub>H<sub>4</sub> and CH<sub>4</sub> at different potentials on PTF(Ni)/Cu and PTF/Cu.<sup>155</sup> (c) A proposed reaction mechanism for the production of CH<sub>4</sub> over CoPC@Zn-N-C.<sup>158</sup> (d) Calculated  $\Delta G$  for the H<sub>2</sub>O dissociation process.<sup>162</sup> (e) Mechanism of CH<sub>3</sub>OH formation on the Rh<sub>1</sub>Cu<sub>4</sub> catalyst.<sup>161</sup>

Wang *et al.* systematically studied the influence of spatial distribution between two components on the tandem reaction process.<sup>157</sup> They chose CoPC molecules, known as excellent CO-producing small molecule catalysts, and Cu nanocubes (Cu<sub>cub</sub>) as a model, and prepared two distinct mixed catalysts. One catalyst was CoPC-Cu<sub>cub</sub>/C, where CoPC and Cu<sub>cub</sub> shared an interface; the other was CoPC-C/Cu<sub>cub</sub>, where CoPC was initially loaded onto carbon black and subsequently mixed with Cu<sub>cub</sub>. Electrochemical tests revealed that CoPC-Cu<sub>cub</sub>/C exhibited nearly double the selectivity for C<sub>2</sub> products compared to Cu<sub>cub</sub>/C, whereas the faradaic efficiency of CoPC-C/Cu<sub>cub</sub> decreased by half. This outcome elucidates the surface transport mechanism of CO intermediates between the two components of the tandem catalyst, highlighting the importance of their relative spatial distribution for achieving efficient tandem

reactions. In addition to the tandem systems between single atoms and metal Cu, tandem catalytic pathways can also be formed between different single-atom sites. For instance, Lin *et al.* reported a tandem catalytic system using CoPC and Zn-N-C for the deep hydrogenation reduction of CO<sub>2</sub> to produce methane.<sup>158</sup> The research results demonstrated that CO<sub>2</sub> was initially reduced to CO on CoPC, then diffused to Zn-N-C, where it undergoes further reduction to CH<sub>4</sub> at the ZnN<sub>4</sub> site (Fig. 8c). Compared to using CoPC or Zn-N-C alone, the tandem catalyst showed more than 100-fold increase in the CH<sub>4</sub>/CO production rate ratio.

**4.3.2 SACs serving as water activation centers.** The selectivity of specific products is also influenced by the rate-determining step dominated by PCET for the formation of key intermediates. For instance, \*CO protonation to \*CHO for methanol, methane,



or ethylene production; and  $^*\text{HC-COH}$  protonation to  $^*\text{HC-CHOH}$  for the production of  $\text{CH}_3\text{CH}_2\text{OH}$ .<sup>20,159,160</sup> These processes are closely related to the coverage of adsorbed protons ( $^*\text{H}_{\text{ad}}$ ), which typically originate from the dissociation of water molecules. Therefore, the introduction of atomically dispersed water activation sites can facilitate the dissociation of water molecules to optimize  $^*\text{H}_{\text{ad}}$  coverage, thereby promoting the generation of key intermediates. In comparison to metal clusters or particles, atomically dispersed sites may have the advantage of avoiding an excessive increase in  $^*\text{H}_{\text{ad}}$  coverage, which could otherwise lead to the promotion of the HER side reaction.<sup>161</sup>

On the reaction pathway of  $\text{CO}_2$  reduction to  $\text{CH}_4$ , the further hydrogenation of the intermediate  $^*\text{CO}$  is often considered the rate-determining step, while the slow water dissociation kinetics limits the rate of proton supply, thereby impeding the electrochemical methanation of  $\text{CO}_2$ . To address this issue, Chen *et al.* successfully introduced single-atom Ir into copper-based catalysts, resulting in the synthesis of Ir single-atom-doped  $\text{Cu}_3\text{N/CuO}$  hybrid materials.<sup>162</sup> This hybrid catalyst exhibits exceptionally high methane selectivity and activity (with a 75% methane Faraday efficiency at a current density of  $320 \text{ mA cm}^{-2}$ ), surpassing catalysts lacking Ir single-atom doping. Experimental and theoretical results indicate that Ir single atoms facilitate the dissociation of water into protons and supply them to  $\text{Cu}_3\text{N/CuO}$  sites for the protonation of  $^*\text{CO}$  to  $^*\text{CHO}$ , significantly accelerating the kinetics of  $\text{CO}_2$  methanation (Fig. 8d). It has been indicated that methanol and methane products share a common intermediate,  $^*\text{CHO}$ . After overcoming the energy barrier of the rate-determining step along the  $\text{C}_1$  pathway (*i.e.*,  $^*\text{CO}$  to  $^*\text{CHO}$ ), the critical branching step for generating methanol or methane involves either continued hydrogenation (resulting in  $^*\text{CHOH}$ ,  $^*\text{CH}_2\text{OH}$ ) or dehydroxylation (leading to  $^*\text{CH}$ ,  $^*\text{CH}_2$ , *etc.*).<sup>163,164</sup> Therefore, further optimizing the  $^*\text{H}$  adsorption on the catalyst surface shows promise for enhancing methanol selectivity. Building on this insight, Zhang *et al.* synthesized a Rh-doped  $\text{Rh}_1\text{Cu}_4$  single-atom alloy catalyst.<sup>161</sup> DFT results demonstrate that isolated Rh sites enhance  $^*\text{H}$  coverage on the  $\text{Rh}_1\text{Cu}_4$  catalyst and facilitate the hydrogenation of  $^*\text{CH}_2\text{OH}$ , leading to methanol production. The  $\text{Rh}_1\text{Cu}_4$  catalyst exhibits the highest methanol partial current density of  $111.7 \pm 12.8 \text{ mA cm}^{-2}$  with a Faraday efficiency of  $46.2 \pm 5.3\%$ . Furthermore, comparative experiments reveal that the introduction of Rh clusters results in excessive  $^*\text{H}$  coverage on the catalyst surface, leading to a decrease in methanol selectivity and an increase in hydrogen production (Fig. 8e). This further shows the advantage of single-atom sites as water activation or  $^*\text{H}$  adsorption sites.

In summary, SACs can promote the supply of CO and protons during the  $\text{CO}_2\text{RR}$  process by facilitating the generation of CO and the dissociation of water. Subsequently, these intermediate products can be captured by another active site in the tandem catalyst, forming  $^*\text{CO}$  and  $^*\text{H}_{\text{ad}}$  species, leading to the acceleration of the rate-determining steps involving C-C coupling and PCET.

#### 4.4 Catalyst support regulation

Choosing the appropriate support material is essential to providing strong binding through ion or covalent interactions,

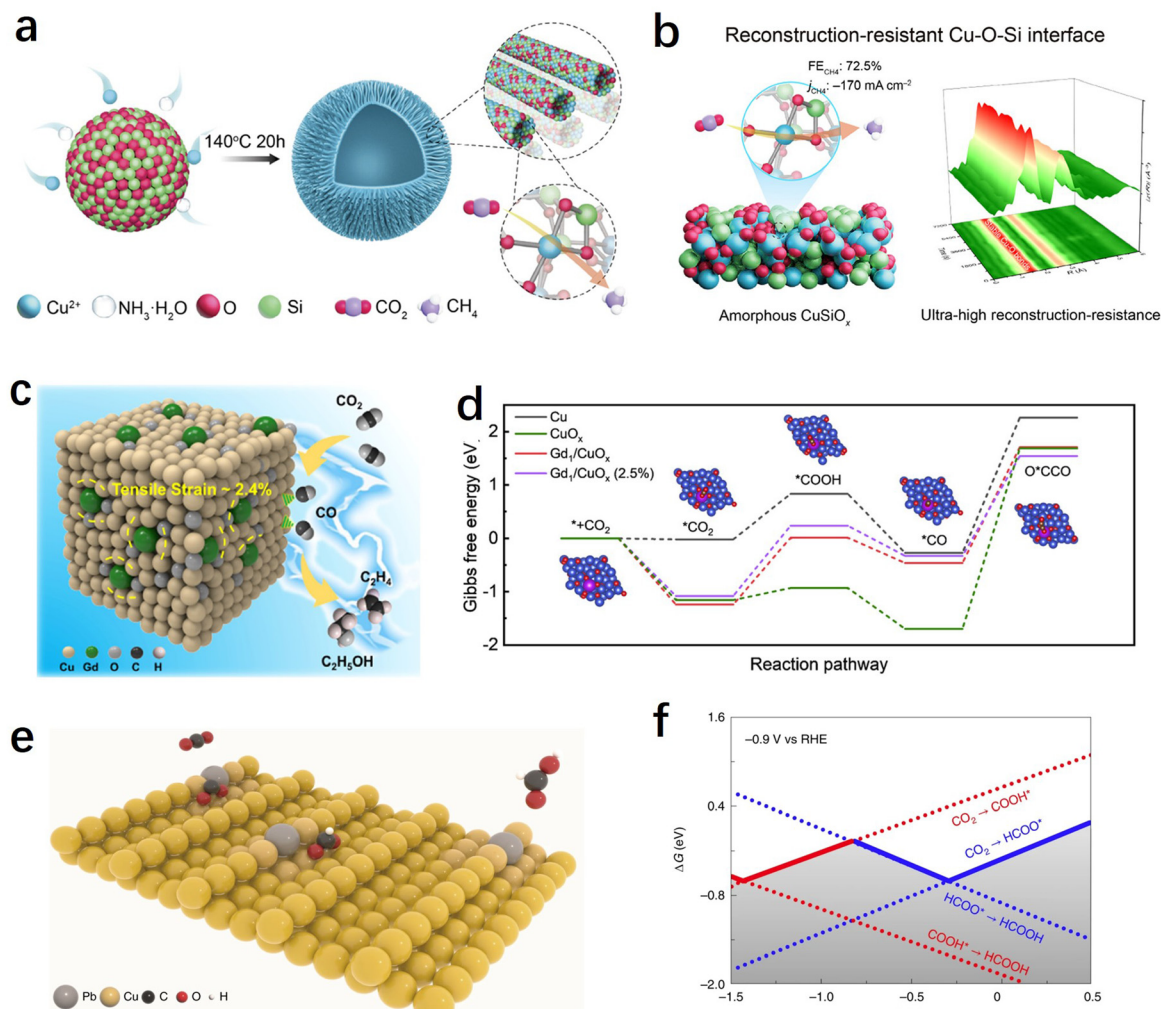
thus securely immobilizing single atoms. Additionally, the specific characteristics of the support can strongly influence the electronic states of SACs, further impacting the catalytic performance of the  $\text{CO}_2\text{RR}$ . The majority of SACs used for the  $\text{CO}_2\text{RR}$  are carbon-based due to their excellent conductivity. Metals, metal oxides, and other supports with unique structural properties and coordination environments can offer more possibilities for tuning the performance of SACs.

We are well aware that copper is the only metal that exhibits appreciable activity towards the multi-electron transfer hydrocarbon products. In particular, Cu SACs exhibited distinct performance compared to non-Cu-based SACs in the generation of products such as methane, ethylene, acetone, *etc.*<sup>82</sup> However, Cu SACs usually undergo reconstruction involving atomic re-arrangement and compositional change during the  $\text{CO}_2\text{RR}$  process, and this uncontrollable electrochemical reconstruction not only leads to the inherently poor stability of Cu-based SACs, but also makes the investigation of real active sites and the establishment of structure-performance relationships shrouded in fog. Traditional carbon-based supports have shown some limitations in stabilizing atomically dispersed metal Cu.<sup>165</sup> Therefore, there is an urgent need to develop novel supports that can stabilize copper-based SACs to advance the field of  $\text{CO}_2\text{RRs}$ . Recently, inspired by traditional  $\text{Cu/SiO}_2$  heterogeneous catalysts, Tan *et al.* have developed a method to stabilize atomic Cu by constructing a Cu-O-Si interface (Fig. 9a).<sup>166</sup> The as-prepared  $\text{CuSiO}_x$  catalyst achieved an efficient electrochemical  $\text{CO}_2$  methanation with a high faradaic efficiency of  $\text{CH}_4$  (72.5% at  $-1.27 \text{ V vs. RHE}$ ) and excellent stability. To address the issue of poor conductivity of the oxide-based support, the authors also assembled a flow-cell device and achieved a remarkable  $\text{CO}_2$ -to- $\text{CH}_4$  conversion rate of  $0.22 \mu\text{mol cm}^{-2} \text{ s}^{-1}$ . More importantly, *in situ* X-ray absorption spectrum experiments indicated that the atomic Cu-O-Si interfacial sites exhibited ultra-high electrochemical stability and reconstruction-resistance over a broad potential window or long-time potentiostatic electrolysis, which attribute to the strong interactions between Cu and silica (Fig. 9b). Using  $\text{CeO}_2$  as a support to enhance the stability of Cu is also a feasible approach. Zhou *et al.* reported a  $\text{CeO}_x$ -stabilized  $\text{Cu}^{2+}$  strategy ( $\text{Cu-CeO}_x$ ) in which  $\text{CeO}_2$  acts as a self-sacrificing component to protect the atomic  $\text{Cu}^{2+}$  active species.<sup>167</sup> They found that after  $\text{CO}_2\text{RRs}$ , the concentration of  $\text{Ce}^{3+}$  in  $\text{Cu-CeO}_x$  increased significantly, as evidenced by *in situ* Raman spectroscopy experiments, indicating that electrons preferentially reduce  $\text{Ce}^{4+}$  to  $\text{Ce}^{3+}$  in  $\text{Cu-CeO}_x$ . Meanwhile, the newly formed  $\text{Ce}^{3+}/\text{Ce}^{4+}$  couple acts as a conductive network to enhance the conductivity of the overall solid solution. It can accelerate electron transfer and suppress the accumulation of electrons at  $\text{Cu}^{2+}$  sites, preventing them from self-reduction.

Oxygen vacancies or Lewis acid sites on metal oxides can also be utilized to modulate the activity of SACs. For instance, Wang *et al.* found that a single Cu atom substituted on the  $\text{CeO}_2(110)$  surface could stably enrich three oxygen vacancies around each Cu site, leading to an efficient  $\text{CO}_2$  adsorption and activation center that promotes methane production.<sup>106</sup>







**Fig. 9** (a) Schematic illustration of the CuSiO<sub>x</sub> synthetic process.<sup>166</sup> (b) The table of contents for the CuSiO<sub>x</sub> catalyst during the CO<sub>2</sub>RR (including the schematic illustration and characterization of the reconstruction-resistance, and the CO<sub>2</sub>RR performance).<sup>166</sup> (c) Illustration of C<sub>2+</sub> product generation promoted by stress engineering in Gd/CuO<sub>x</sub>.<sup>171</sup> (d) Gibbs free energy diagrams of CO<sub>2</sub> reduction to O\*CCO on surfaces of Cu, CuO<sub>x</sub>, Gd<sub>1</sub>/CuO<sub>x</sub>, and Gd<sub>1</sub>/CuO<sub>x</sub> (2.5%).<sup>171</sup> (e) Schematic illustration of CO<sub>2</sub> conversion into HCOOH over Pb<sub>1</sub>Cu single-atom alloys.<sup>38</sup> (f) One-dimensional RPD for the CO<sub>2</sub>RR. The solid lines show the G<sub>RPD</sub>-limiting steps for the more favoured COOH\* path and the HCOO\* path.<sup>38</sup>

Chen *et al.* have demonstrated through theoretical predictions that the Lewis acid sites in metal oxides such as Al<sub>2</sub>O<sub>3</sub> and Cr<sub>2</sub>O<sub>3</sub> not only facilitate the activation of CO<sub>2</sub> but also lower the energy barrier for the \*CH<sub>4</sub>O intermediate, providing a favourable pathway for methane production.<sup>168</sup> Based on these findings, the authors synthesized Cu SACs supported on ultrathin Al<sub>2</sub>O<sub>3</sub> nanosheets with strong Lewis acid sites. The catalyst exhibited an excellent electrochemical CO<sub>2</sub>→CH<sub>4</sub> conversion performance, with a methane faradaic efficiency of 62% at −1.2 V vs. RHE. Yin *et al.* demonstrated that strong binding sites for CO<sub>2</sub> adsorption can be formed at the Cu–CeO<sub>2</sub> interface, promoting CO<sub>2</sub> activation and conversion into \*CO intermediates on the nearby Cu surface.<sup>169</sup> As the Cu loading increases, the CO<sub>2</sub> reduction product can be tailored from C<sub>1</sub> to C<sub>2+</sub>.

Using Cu-based materials as supports (such as metallic copper or copper oxides) and introducing atomically dispersed

heteroatoms into Cu is a highly effective approach for modulating the activity of Cu-based catalysts. Previous researches have indicated that Cu<sup>+</sup> sites played a crucial role in improving the selectivity of C<sub>2+</sub> products.<sup>170</sup> It can not only enhance the CO adsorption and facilitate C–C coupling reactions but also stabilize C<sub>2</sub> intermediates. However, Cu<sup>+</sup> was found to be unstable under negative potentials during the CO<sub>2</sub>RR process. Feng *et al.* synthesized Gd-doped CuO<sub>x</sub> catalyst (Gd<sub>1</sub>/CuO<sub>x</sub>) using a simple one-step solvent thermal method.<sup>171</sup> The research findings demonstrated that atomically dispersed Gd can stabilize Cu<sup>+</sup> and induce tensile strain in the catalyst. The prepared Gd<sub>1</sub>/CuO<sub>x</sub> exhibited excellent performance in CO<sub>2</sub>-to-C<sub>2+</sub> product conversion, achieving a faradaic efficiency of 81.4% for C<sub>2+</sub> products at −0.8 V. Experimental and computational results suggested that Gd doping improved the stability of the crucial intermediate O\*CCO, reduced the energy barrier for C–C coupling, and resulted in high CO<sub>2</sub>RR-to-C<sub>2+</sub> product

performance (Fig. 9c and d). Zheng *et al.* synthesized a Pb-alloyed Cu catalyst, denoted as Pb<sub>1</sub>Cu, by incorporating Pb single atoms onto the surface of metallic copper (Fig. 9e).<sup>38</sup> The introduction of Pb had a significant impact on the protonation process during the CO<sub>2</sub>RR. Rather than occurring on the oxygen site, the initial protonation was observed to preferentially take place on the carbon site of CO<sub>2</sub> when Pb was present. This led to the formation of the \*HCOO pathway instead of the \*COOH pathway, resulting in Pb<sub>1</sub>Cu demonstrating exceptional formate activity with an ultra-high faradaic efficiency of approximately 96% at current densities exceeding 1 A cm<sup>-2</sup> (Fig. 9f). Moreover, the researchers utilized the Pb<sub>1</sub>Cu catalyst to construct a solid electrolyte reactor, enabling the continuous production of pure formic acid solution for a remarkable duration of 180 hours, while maintaining a high current density above 100 mA cm<sup>-2</sup>. These findings highlight the potential of Pb<sub>1</sub>Cu as a promising catalyst for the CO<sub>2</sub>RR and its application in the efficient and sustained production of formic acid.

In conclusion, adjusting the type, composition, and structure of the supports can optimize the electronic and geometric properties of SACs, enhancing the catalytic activity and stability. This holds significant importance for the efficient, stable, and sustainable development of SACs for the CO<sub>2</sub>RR.

## 5. Conclusions and perspectives

The unique geometric/electronic structures of SACs qualify them as a new family of catalytic materials and a new frontier in the research field of CO<sub>2</sub>RRs. In this review, we introduced the research status of SACs and summarized the synthesis strategies for SACs. Furthermore, we briefly introduced the fundamental parameters in the CO<sub>2</sub>RR and attempted to summarize the possible reaction mechanisms for generating C<sub>1</sub> and C<sub>2</sub> products in the CO<sub>2</sub>RR. Most importantly, we focused on discussing the structure–function relationship between the structure of SACs and the performance of CO<sub>2</sub>RR, mainly manifested in the following four aspects of regulation: coordination environment regulation, diatomic sites regulation, tandem catalytic regulation, and catalyst support regulation. Although significant progress has been made in the synthesis of SACs as well as in the application of SACs in the CO<sub>2</sub>RR and the establishment of their structure–function relationships, there are still certain limitations or challenges to the practical application of SACs in CO<sub>2</sub>RRs. Summarized below are some potential research directions and challenges for SACs in CO<sub>2</sub>RR applications in the future (Fig. 10).

### 1. Precise synthesis and characterization of SACs

The precise synthesis of SACs has always been a challenge for their application in various fields, including the CO<sub>2</sub>RR. Metal single atoms are often fixed by the coordination of heteroatoms on the support owing to their high surface free energy. At present, the preparation of SACs often resorts to high-temperature calcination steps, which may lead to a certain degree of randomness in the generation of SACs. Many studies

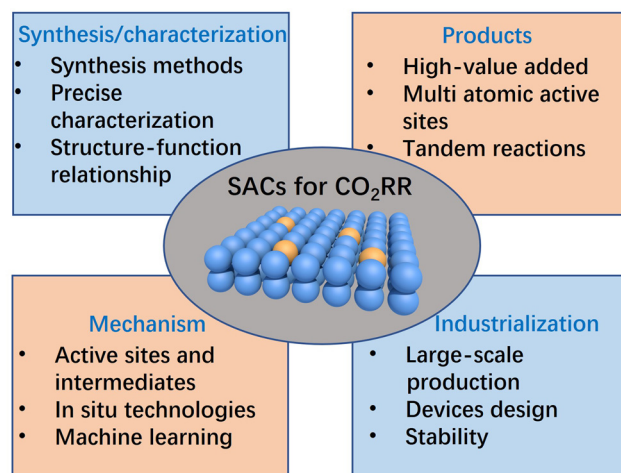


Fig. 10 Schematic illustration of future directions and challenges of SACs for the CO<sub>2</sub>RR.

have shown that minor alterations in calcination temperature can lead to major changes in the coordination environment of SACs, and needless to say, their catalytic activity also changes accordingly. Therefore, when a high-temperature calcination step is used to prepare SACs, strict control of calcination conditions is necessary to ensure the repeatability of the preparation of different batches of catalysts. Obviously, a more precise strategy for preparing SACs has always been pursued, especially for the preparation of high-loading SACs, which currently faces greater difficulties. In addition, as the research on SACs in different applications deepens, there is increasing interest on multi-site catalysts (such as DACs). However, research on DACs is currently still in its early stages, and many basic concepts and standards have yet to be established. For instance, the characterization of SACs mainly depends on AC-HAADF-STEM and XAS technologies. AC-HAADF-STEM records the projected images of metal single atoms under the incident electron beam, and cannot distinguish the spatial arrangement of metal single atoms in close proximity; on the other hand, XAS records the average signal of the test sample, and cannot separate the information of a single active site. The limitations of these characterization techniques are particularly prominent in the analysis of DACs. Especially in the AC-HAADF-STEM images of DACs, the spatial arrangement of adjacent metal atoms cannot be determined by simply reading the high-contrast bright spots in the projected image while ignoring their spatial relationship along the incident electron beam. In this regard, one of our recent works attempts to identify “true/false” DACs by using *in situ* rotation operation in AC-HAADF-STEM characterization.<sup>172</sup> Therefore, more precise synthesis strategies and more advanced characterization methods need to be further explored, as the precise synthesis and characterization of SACs are prerequisites for understanding their structure–function relationship.

### 2. Rational design of SACs for producing non-CO products

As summarized in this review, considerably satisfactory CO selectivity has been achieved from the CO<sub>2</sub>RR over a number of SACs, such as Fe, Ni, Mn, and Ag, but it still poses a great



challenge for high-value-added products beyond CO. There are two main reasons for this: (1) on the one hand, a single metal active site has moderate binding strength to the intermediate of CO<sub>2</sub>RR, especially \*COOH and \*CO. Thus, \*CO has a moderate desorption energy barrier, which is beneficial for the production of CO. (2) On the other hand, the atomically dispersed metal active sites are isolated from each other, leading to the physical separation of the intermediates, thus blocking further C–C coupling. Owing to its complex reaction mechanism and diverse reaction pathways, it is rather difficult to precisely control the distribution of the reaction products in the CO<sub>2</sub>RR. In order to expand the product range of the CO<sub>2</sub>RR and to obtain high-value-added products, two promising strategies could be explored. One is to rationally design DACs with multiple reaction active sites, which can provide mutually related synergistic active sites. The interrelated multiple active sites could provide a heteroatomic interface for asymmetric C–C coupling, which is expected to yield specific multi-carbon (C<sub>2+</sub>) products. Another effective strategy is to construct tandem catalytic systems. The general principle is to combine SACs with high CO selectivity with Cu-based catalysts to achieve continuous conversion of CO<sub>2</sub> to CO and further to multi-carbon products, thus achieving high C<sub>2+</sub> Faraday efficiencies. This method can promote the transfer of reaction intermediates and electrons, thereby improving reaction efficiency and selectivity. In addition, the tandem catalytic system lessens the difficulties in the catalyst design, and makes the catalytic reaction more controllable and predictable.

### 3. Deciphering the catalytic mechanisms of CO<sub>2</sub>RRs

At present, significant progress has been made in both the synthesis of SACs and their application in CO<sub>2</sub>RRs. However, owing to the diverse reaction pathways and complex reaction intermediates, the dynamic process and reaction mechanism of the CO<sub>2</sub>RR are still difficult to understand. The catalytic activity of the CO<sub>2</sub>RR is highly dependent on its active sites; therefore, the structure of the active site and its dynamic evolution during the catalytic reaction process are crucial. However, conventional characterization methods often detect the state of catalysts or catalytic reactions at a certain point in time but cannot monitor their dynamic evolution process. Therefore, it would be very helpful to use *in situ* technologies to identify the dynamic evolution of active sites and capture catalytic reaction intermediates, but this also requires more stringent test conditions. Currently, *in situ* tests are often conducted separately, such as *in situ* XAS, *in situ* TEM, and *in situ* Raman. It is expected that more advanced coupled *in situ* test techniques could be developed in the future to facilitate in-depth exploration of reaction mechanisms. In addition, machine learning has made significant progress in the preparation of nano-materials and its application in the CO<sub>2</sub>RR, and it is expected to be introduced into the construction and performance prediction of SACs in the future. Machine learning can achieve high-throughput material performance prediction and assist in analyzing catalytic mechanisms, thus greatly reducing the trial-and-error costs.

### 4. Industrial-level applications

The industrial application of SACs in the CO<sub>2</sub>RR is mainly focused on two aspects: large-scale synthesis of SACs and industrial-level performance of SACs in the CO<sub>2</sub>RR. At present, a number of methods have been developed in the laboratory for the preparation of SACs, but a significant proportion of these methods are rather complex and cumbersome. The complex or harsh preparation conditions would result in poor repeatability of SACs preparation, thereby limiting its large-scale production. Moreover, apart from considerations regarding its repeatability, large-scale production of SACs also needs to balance economic benefits, which drives the preparation of SACs towards simpler, more efficient, and more reliable directions. On the other hand, in addition to achieving industrial-level preparation, SACs also need to meet industrial-level test conditions and performance indicators. As we already know, the low solubility of CO<sub>2</sub> in aqueous electrolytes greatly constrains its mass transport at high current densities, which is also a bottleneck for the industrialization of the CO<sub>2</sub>RR. To address these issues, it has been attempted to combine SACs with gas diffusion layers and the assembly of membrane electrode components in flow cells, which helps to meet the requirements of industrial-level reactions and has made some notable progress thus far. However, reactors often fail during operation owing to various problems such as catalyst aggregation and membrane flooding, and these issues still need to be addressed one by one in future device design. In addition, the stability of SACs is also one of the evaluation metrics for their potentials of industrialization. Currently, the research on SACs in the CO<sub>2</sub>RR is mainly focused on catalytic activity and selectivity, while stability tests often fail to meet the industrial requirements. Therefore, it is necessary to strengthen the research on catalyst stability in the future, to explore the deactivation mechanism of catalysts, and to design efficient SACs that feature balanced activity, selectivity, and stability.

### Conflicts of interest

There are no conflicts to declare.

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### Notes and references

- 1 S. Chu, Y. Cui and N. Liu, *Nat. Mater.*, 2016, **16**, 16–22.
- 2 S. Gao, Y. Lin, X. Jiao, Y. Sun, Q. Luo, W. Zhang, D. Li, J. Yang and Y. Xie, *Nature*, 2016, **529**, 68–71.
- 3 S. Chu and A. Majumdar, *Nature*, 2012, **488**, 294–303.
- 4 D. R. Feldman, W. D. Collins, P. J. Gero, M. S. Torn, E. J. Mlawer and T. R. Shippert, *Nature*, 2015, **519**, 339–343.





- 5 H.-Y. Kuang, Y.-X. Lin, X.-H. Li and J.-S. Chen, *J. Mater. Chem. A*, 2021, **9**, 20857–20873.
- 6 A. Seiff and D. B. Kirk, *J. Geophys. Res.*, 1977, **82**, 4364–4378.
- 7 V. G. Dovì, F. Friedler, D. Huisinigh and J. J. Klemeš, *J. Cleaner Prod.*, 2009, **17**, 889–895.
- 8 Z. Yuan, M. R. Eden and R. Gani, *Ind. Eng. Chem. Res.*, 2015, **55**, 3383–3419.
- 9 E. S. Sanz-Perez, C. R. Murdock, S. A. Didas and C. W. Jones, *Chem. Rev.*, 2016, **116**, 11840–11876.
- 10 H. Herring, *Energy*, 2006, **31**, 10–20.
- 11 C. Costentin, M. Robert and J.-M. Savéant, *Chem. Soc. Rev.*, 2013, **42**, 2423–2436.
- 12 E. V. Kondratenko, G. Mul, J. Baltrusaitis, G. O. Larrazábal and J. Pérez-Ramírez, *Energy Environ. Sci.*, 2013, **6**, 3112–3135.
- 13 J. Qiao, Y. Liu, F. Hong and J. Zhang, *Chem. Soc. Rev.*, 2014, **43**, 631–675.
- 14 M. Bevilacqua, J. Filippi, H. A. Miller and F. Vizza, *Energy Technol.*, 2015, **3**, 197–210.
- 15 Y. Li, S. H. Chan and Q. Sun, *Nanoscale*, 2015, **7**, 8663–8683.
- 16 W. H. Wang, Y. Himeda, J. T. Muckerman, G. F. Manbeck and E. Fujita, *Chem. Rev.*, 2015, **115**, 12936–12973.
- 17 M. Li, H. Wang, W. Luo, P. C. Sherrell, J. Chen and J. Yang, *Adv. Mater.*, 2020, **32**, e2001848.
- 18 H. Gu, J. Wu and L. Zhang, *Nano Res.*, 2022, **15**, 9747–9763.
- 19 T. N. Nguyen, M. Salehi, Q. V. Le, A. Seifitokaldani and C. T. Dinh, *ACS Catal.*, 2020, **10**, 10068–10095.
- 20 X. Tan, Z. Zhuang, Y. Zhang, K. Sun and C. Chen, *Chem. Commun.*, 2023, **59**, 2682–2696.
- 21 S. Wang, L. Wang, D. Wang and Y. Li, *Energy Environ. Sci.*, 2023, **16**, 2759–2803.
- 22 M. Schreier, F. Héroguel, L. Steier, S. Ahmad, J. S. Luterbacher, M. T. Mayer, J. Luo and M. Grätzel, *Nat. Energy*, 2017, **2**, 17087.
- 23 K. Li, B. Peng and T. Peng, *ACS Catal.*, 2016, **6**, 7485–7527.
- 24 Y. Wang, Y. Liu, W. Liu, J. Wu, Q. Li, Q. Feng, Z. Chen, X. Xiong, D. Wang and Y. Lei, *Energy Environ. Sci.*, 2020, **13**, 4609–4624.
- 25 S. G. Han, D. D. Ma and Q. L. Zhu, *Small Methods*, 2021, **5**, e2100102.
- 26 Y. Wang, P. Han, X. Lv, L. Zhang and G. Zheng, *Joule*, 2018, **2**, 2551–2582.
- 27 Y. Cheng, S. Yang, S. P. Jiang and S. Wang, *Small Methods*, 2019, **3**, 1800440.
- 28 C. Cao, D. D. Ma, J. Jia, Q. Xu, X. T. Wu and Q. L. Zhu, *Adv. Mater.*, 2021, **33**, e2008631.
- 29 C. J. Peng, G. Zeng, D. D. Ma, C. Cao, S. Zhou, X. T. Wu and Q. L. Zhu, *ACS Appl. Mater. Interfaces*, 2021, **13**, 20589–20597.
- 30 Y. Zhao, X. Tan, W. Yang, C. Jia, X. Chen, W. Ren, S. C. Smith and C. Zhao, *Angew. Chem., Int. Ed.*, 2020, **59**, 21493–21498.
- 31 R. M. Arán-Ais, F. Scholten, S. Kunze, R. Rizo and B. Roldan Cuenya, *Nat. Energy*, 2020, **5**, 317–325.
- 32 D. Zhong, Z. J. Zhao, Q. Zhao, D. Cheng, B. Liu, G. Zhang, W. Deng, H. Dong, L. Zhang, J. Li, J. Li and J. Gong, *Angew. Chem., Int. Ed.*, 2021, **60**, 4879–4885.
- 33 W. Zhang, Q. Qin, L. Dai, R. Qin, X. Zhao, X. Chen, D. Ou, J. Chen, T. T. Chuong, B. Wu and N. Zheng, *Angew. Chem., Int. Ed.*, 2018, **57**, 9475–9479.
- 34 A. Eilert, F. S. Roberts, D. Friebe and A. Nilsson, *J. Phys. Chem. Lett.*, 2016, **7**, 1466–1470.
- 35 L.-P. Yuan, W.-J. Jiang, X.-L. Liu, Y.-H. He, C. He, T. Tang, J. Zhang and J.-S. Hu, *ACS Catal.*, 2020, **10**, 13227–13235.
- 36 Z. Chen, M.-R. Gao, N. Duan, J. Zhang, Y.-Q. Zhang, T. Fan, J. Zhang, Y. Dong, J. Li, Q. Liu, X. Yi and J.-L. Luo, *Appl. Catal., B*, 2020, **277**, 119252.
- 37 T. Yuan, Z. Hu, Y. Zhao, J. Fang, J. Lv, Q. Zhang, Z. Zhuang, L. Gu and S. Hu, *Nano Lett.*, 2020, **20**, 2916–2922.
- 38 T. Zheng, C. Liu, C. Guo, M. Zhang, X. Li, Q. Jiang, W. Xue, H. Li, A. Li, C. W. Pao, J. Xiao, C. Xia and J. Zeng, *Nat. Nanotechnol.*, 2021, **16**, 1386–1393.
- 39 H. Xie, Y. Wan, X. Wang, J. Liang, G. Lu, T. Wang, G. Chai, N. M. Adli, C. Priest, Y. Huang, G. Wu and Q. Li, *Appl. Catal., B*, 2021, **289**, 119783.
- 40 T. Shen, S. Wang, T. Zhao, Y. Hu and D. Wang, *Adv. Energy Mater.*, 2022, **12**, 2201823.
- 41 R. T. Hannagan, G. Giannakakis, M. Flytzani-Stephanopoulos and E. C. H. Sykes, *Chem. Rev.*, 2020, **120**, 12044–12088.
- 42 M. E. Ahmed, S. Adam, D. Saha, J. Fize, V. Artero, A. Dey and C. Duboc, *ACS Energy Lett.*, 2020, **5**, 3837–3842.
- 43 J. Xu, S. Lai, M. Hu, S. Ge, R. Xie, F. Li, D. Hua, H. Xu, H. Zhou, R. Wu, J. Fu, Y. Qiu, J. He, C. Li, H. Liu, Y. Liu, J. Sun, X. Liu and J. Luo, *Small Methods*, 2020, **4**, 2000567.
- 44 Z. Chen, X. Zhang, M. Jiao, K. Mou, X. Zhang and L. Liu, *Adv. Energy Mater.*, 2020, **10**, 1903664.
- 45 X. Ma, J. Du, H. Sun, F. Ye, X. Wang, P. Xu, C. Hu, L. Zhang and D. Liu, *Appl. Catal., B*, 2021, **298**, 120543.
- 46 A. Vasileff, Y. Zheng and S. Z. Qiao, *Adv. Energy Mater.*, 2017, **7**, 1700759.
- 47 C. Chen, X. Sun, X. Yan, Y. Wu, H. Liu, Q. Zhu, B. B. A. Bediako and B. Han, *Angew. Chem., Int. Ed.*, 2020, **59**, 11123–11129.
- 48 W. Zhu and C. Chen, *Chem*, 2019, **5**, 2737–2739.
- 49 A. Wang, J. Li and T. Zhang, *Nat. Rev. Chem.*, 2018, **2**, 65–81.
- 50 X. Liang, N. Fu, S. Yao, Z. Li and Y. Li, *J. Am. Chem. Soc.*, 2022, **144**, 18155–18174.
- 51 B. Qiao, A. Wang, X. Yang, L. F. Allard, Z. Jiang, Y. Cui, J. Liu, J. Li and T. Zhang, *Nat. Chem.*, 2011, **3**, 634–641.
- 52 S. Zhang, X. Ao, J. Huang, B. Wei, Y. Zhai, D. Zhai, W. Deng, C. Su, D. Wang and Y. Li, *Nano Lett.*, 2021, **21**, 9691–9698.
- 53 N. Fu, X. Liang, Z. Li, W. Chen, Y. Wang, L. Zheng, Q. Zhang, C. Chen, D. Wang, Q. Peng, L. Gu and Y. Li, *Nano Res.*, 2020, **13**, 947–951.
- 54 J. Zhang, Y. Zhao, X. Guo, C. Chen, C.-L. Dong, R.-S. Liu, C.-P. Han, Y. Li, Y. Gogotsi and G. Wang, *Nat. Catal.*, 2018, **1**, 985–992.
- 55 Q. Li, Z. Li, Q. Zhang, L. Zheng, W. Yan, X. Liang, L. Gu, C. Chen, D. Wang, Q. Peng and Y. Li, *Nano Res.*, 2020, **14**, 1435–1442.





- 56 J. Yang, W. H. Li, S. Tan, K. Xu, Y. Wang, D. Wang and Y. Li, *Angew. Chem., Int. Ed.*, 2021, **60**, 19085–19091.
- 57 Y. Chen, S. Ji, C. Chen, Q. Peng, D. Wang and Y. Li, *Joule*, 2018, **2**, 1242–1264.
- 58 S. Ji, Y. Chen, X. Wang, Z. Zhang, D. Wang and Y. Li, *Chem. Rev.*, 2020, **120**, 11900–11955.
- 59 S. Meshitsuka, M. Ichikawa and K. Tamaru, *J. Chem. Soc., Chem. Commun.*, 1974, 158–159.
- 60 Z. Sun, T. Ma, H. Tao, Q. Fan and B. Han, *Chem*, 2017, **3**, 560–587.
- 61 R. Li and D. Wang, *Adv. Energy Mater.*, 2022, **12**, 2103564.
- 62 H. Liu, H. Rong and J. Zhang, *ChemSusChem*, 2022, **15**, e202200498.
- 63 Q. An, J. Jiang, W. Cheng, H. Su, Y. Jiang and Q. Liu, *Small Methods*, 2022, **6**, e2200408.
- 64 Y. Ying, X. Luo, J. Qiao and H. Huang, *Adv. Funct. Mater.*, 2020, **31**, 2007423.
- 65 Y. Hu, Z. Li, B. Li and C. Yu, *Small*, 2022, **18**, e2203589.
- 66 Y. N. Gong, C. Y. Cao, W. J. Shi, J. H. Zhang, J. H. Deng, T. B. Lu and D. C. Zhong, *Angew. Chem., Int. Ed.*, 2022, **61**, e202215187.
- 67 W. Zhang, Y. Chao, W. Zhang, J. Zhou, F. Lv, K. Wang, F. Lin, H. Luo, J. Li, M. Tong, E. Wang and S. Guo, *Adv. Mater.*, 2021, **33**, e2102576.
- 68 F. Pan and Y. Yang, *Energy Environ. Sci.*, 2020, **13**, 2275–2309.
- 69 H. Rabiee, L. Ge, X. Zhang, S. Hu, M. Li and Z. Yuan, *Energy Environ. Sci.*, 2021, **14**, 1959–2008.
- 70 R. Kortlever, J. Shen, K. J. Schouten, F. Calle-Vallejo and M. T. Koper, *J. Phys. Chem. Lett.*, 2015, **6**, 4073–4082.
- 71 J. Rosen, G. S. Hutchings, Q. Lu, S. Rivera, Y. Zhou, D. G. Vlachos and F. Jiao, *ACS Catal.*, 2015, **5**, 4293–4299.
- 72 W. Ju, A. Bagger, G. P. Hao, A. S. Varela, I. Sinev, V. Bon, B. Roldan Cuenya, S. Kaskel, J. Rossmeisl and P. Strasser, *Nat. Commun.*, 2017, **8**, 944.
- 73 T. K. Todorova, M. W. Schreiber and M. Fontecave, *ACS Catal.*, 2019, **10**, 1754–1768.
- 74 S. Vijay, W. Ju, S. Brückner, S.-C. Tsang, P. Strasser and K. Chan, *Nat. Catal.*, 2021, **4**, 1024–1031.
- 75 A. A. Peterson, F. Abild-Pedersen, F. Studt, J. Rossmeisl and J. K. Nørskov, *Energy Environ. Sci.*, 2010, **3**, 1311–1315.
- 76 X. Nie, M. R. Esopi, M. J. Janik and A. Asthagiri, *Angew. Chem., Int. Ed.*, 2013, **52**, 2459–2462.
- 77 Z. Pan, K. Wang, K. Ye, Y. Wang, H.-Y. Su, B. Hu, J. Xiao, T. Yu, Y. Wang and S. Song, *ACS Catal.*, 2020, **10**, 3871–3880.
- 78 G. Wang, J. Chen, Y. Ding, P. Cai, L. Yi, Y. Li, C. Tu, Y. Hou, Z. Wen and L. Dai, *Chem. Soc. Rev.*, 2021, **50**, 4993–5061.
- 79 H. Mistry, A. S. Varela, C. S. Bonifacio, I. Zegkinoglou, I. Sinev, Y. W. Choi, K. Kisslinger, E. A. Stach, J. C. Yang, P. Strasser and B. R. Cuenya, *Nat. Commun.*, 2016, **7**, 12123.
- 80 T. T. H. Hoang, S. Ma, J. I. Gold, P. J. A. Kenis and A. A. Gewirth, *ACS Catal.*, 2017, **7**, 3313–3321.
- 81 B. Zhang, B. Zhang, Y. Jiang, T. Ma, H. Pan and W. Sun, *Small*, 2021, **17**, e2101443.
- 82 K. Zhao, X. Nie, H. Wang, S. Chen, X. Quan, H. Yu, W. Choi, G. Zhang, B. Kim and J. G. Chen, *Nat. Commun.*, 2020, **11**, 2455.
- 83 D. Karapinar, N. T. Huan, N. Ranjbar Sahraie, J. Li, D. Wakerley, N. Touati, S. Zanna, D. Taverna, L. H. Galvão Tizei, A. Zitolo, F. Jaouen, V. Mougel and M. Fontecave, *Angew. Chem., Int. Ed.*, 2019, **131**, 15242–15247.
- 84 P. Shao, W. Zhou, Q. L. Hong, L. Yi, L. Zheng, W. Wang, H. X. Zhang, H. Zhang and J. Zhang, *Angew. Chem., Int. Ed.*, 2021, **60**, 16687–16692.
- 85 Q. Liu, J. Ma and C. Chen, *Chin. J. Catal.*, 2022, **43**, 898–912.
- 86 X. Wang, Z. Chen, X. Zhao, T. Yao, W. Chen, R. You, C. Zhao, G. Wu, J. Wang, W. Huang, J. Yang, X. Hong, S. Wei, Y. Wu and Y. Li, *Angew. Chem., Int. Ed.*, 2018, **57**, 1944–1948.
- 87 Y. Zhang, L. Jiao, W. Yang, C. Xie and H. L. Jiang, *Angew. Chem., Int. Ed.*, 2021, **60**, 7607–7611.
- 88 Y. Hou, Y.-L. Liang, P.-C. Shi, Y.-B. Huang and R. Cao, *Appl. Catal., B*, 2020, **271**, 118929.
- 89 L. Jiao, J. Zhu, Y. Zhang, W. Yang, S. Zhou, A. Li, C. Xie, X. Zheng, W. Zhou, S. H. Yu and H. L. Jiang, *J. Am. Chem. Soc.*, 2021, **143**, 19417–19424.
- 90 Q. Cao, L.-L. Zhang, C. Zhou, J.-H. He, A. Marcomini and J.-M. Lu, *Appl. Catal., B*, 2021, **294**, 120238.
- 91 Y. Zhou, L. Chen, L. Sheng, Q. Luo, W. Zhang and J. Yang, *Nano Res.*, 2022, **15**, 7994–8000.
- 92 Y. Zhu, X. Yang, C. Peng, C. Priest, Y. Mei and G. Wu, *Small*, 2021, **17**, e2005148.
- 93 S. Chen, W. H. Li, W. Jiang, J. Yang, J. Zhu, L. Wang, H. Ou, Z. Zhuang, M. Chen, X. Sun, D. Wang and Y. Li, *Angew. Chem., Int. Ed.*, 2022, **61**, e202114450.
- 94 Y. S. Wei, M. Zhang, R. Zou and Q. Xu, *Chem. Rev.*, 2020, **120**, 12089–12174.
- 95 S. Mallakpour, F. Sirous and C. M. Hussain, *Top. Curr. Chem.*, 2021, **380**, 7.
- 96 Q. Hao, H.-x Zhong, J.-z Wang, K.-h Liu, J.-m Yan, Z.-h Ren, N. Zhou, X. Zhao, H. Zhang, D.-x Liu, X. Liu, L.-w Chen, J. Luo and X.-b Zhang, *Nat. Synth.*, 2022, **1**, 719–728.
- 97 J. Fonseca, T. Gong, L. Jiao and H.-L. Jiang, *J. Mater. Chem. A*, 2021, **9**, 10562–10611.
- 98 Y. Yun, H. Zeng, L. Li, H. Li, S. Cheng, N. Sun, M. Li, H. Sheng, S. Hu, T. Yao and M. Zhu, *Adv. Mater.*, 2023, **35**, e2209561.
- 99 B. Xu, H. Wang, W. Wang, L. Gao, S. Li, X. Pan, H. Wang, H. Yang, X. Meng, Q. Wu, L. Zheng, S. Chen, X. Shi, K. Fan, X. Yan and H. Liu, *Angew. Chem., Int. Ed.*, 2019, **131**, 4965–4970.
- 100 Z. Li, Y. Chen, S. Ji, Y. Tang, W. Chen, A. Li, J. Zhao, Y. Xiong, Y. Wu, Y. Gong, T. Yao, W. Liu, L. Zheng, J. Dong, Y. Wang, Z. Zhuang, W. Xing, C. T. He, C. Peng, W. C. Cheong, Q. Li, M. Zhang, Z. Chen, N. Fu, X. Gao, W. Zhu, J. Wan, J. Zhang, L. Gu, S. Wei, P. Hu, J. Luo, J. Li, C. Chen, Q. Peng, X. Duan, Y. Huang, X. M. Chen, D. Wang and Y. Li, *Nat. Chem.*, 2020, **12**, 764–772.
- 101 C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, J. Yang, S. Wei, Y. Wu and Y. Li, *J. Am. Chem. Soc.*, 2017, **139**, 8078–8081.



- 102 X. Jiang, H. Li, J. Xiao, D. Gao, R. Si, F. Yang, Y. Li, G. Wang and X. Bao, *Nano Energy*, 2018, **52**, 345–350.
- 103 Z. Li, D. He, X. Yan, S. Dai, S. Younan, Z. Ke, X. Pan, X. Xiao, H. Wu and J. Gu, *Angew. Chem., Int. Ed.*, 2020, **132**, 18731–18736.
- 104 N. Mohd Adli, W. Shan, S. Hwang, W. Samarakoon, S. Karakalos, Y. Li, D. A. Cullen, D. Su, Z. Feng, G. Wang and G. Wu, *Angew. Chem., Int. Ed.*, 2020, **133**, 1035–1045.
- 105 G. Hai, X. Xue, S. Feng, Y. Ma and X. Huang, *ACS Catal.*, 2022, **12**, 15271–15281.
- 106 Y. Wang, Z. Chen, P. Han, Y. Du, Z. Gu, X. Xu and G. Zheng, *ACS Catal.*, 2018, **8**, 7113–7119.
- 107 C. Jia, S. Li, Y. Zhao, R. K. Hocking, W. Ren, X. Chen, Z. Su, W. Yang, Y. Wang, S. Zheng, F. Pan and C. Zhao, *Adv. Funct. Mater.*, 2021, **31**, 2107072.
- 108 X. Zu, X. Li, W. Liu, Y. Sun, J. Xu, T. Yao, W. Yan, S. Gao, C. Wang, S. Wei and Y. Xie, *Adv. Mater.*, 2019, **31**, e1808135.
- 109 H. Zou, G. Zhao, H. Dai, H. Dong, W. Luo, L. Wang, Z. Lu, Y. Luo, G. Zhang and L. Duan, *Angew. Chem., Int. Ed.*, 2023, **62**, e202217220.
- 110 G. Shi, Y. Xie, L. Du, X. Fu, X. Chen, W. Xie, T. B. Lu, M. Yuan and M. Wang, *Angew. Chem., Int. Ed.*, 2022, **61**, e202203569.
- 111 J. Jiao, R. Lin, S. Liu, W. C. Cheong, C. Zhang, Z. Chen, Y. Pan, J. Tang, K. Wu, S. F. Hung, H. M. Chen, L. Zheng, Q. Lu, X. Yang, B. Xu, H. Xiao, J. Li, D. Wang, Q. Peng, C. Chen and Y. Li, *Nat. Chem.*, 2019, **11**, 222–228.
- 112 Z. Ma, T. Wan, D. Zhang, J. A. Yuwono, C. Tsounis, J. Jiang, Y. H. Chou, X. Lu, P. V. Kumar, Y. H. Ng, D. Chu, C. Y. Toe, Z. Han and R. Amal, *ACS Nano*, 2023, **17**, 2387–2398.
- 113 M. B. Ross, C. T. Dinh, Y. Li, D. Kim, P. De Luna, E. H. Sargent and P. Yang, *J. Am. Chem. Soc.*, 2017, **139**, 9359–9363.
- 114 N. Xuan, J. Chen, J. Shi, Y. Yue, P. Zhuang, K. Ba, Y. Sun, J. Shen, Y. Liu, B. Ge and Z. Sun, *Chem. Mater.*, 2018, **31**, 429–435.
- 115 Z. Wang, J. Yang, J. Cao, W. Chen, G. Wang, F. Liao, X. Zhou, F. Zhou, R. Li, Z. Q. Yu, G. Zhang, X. Duan and Y. Wu, *ACS Nano*, 2020, **14**, 6164–6172.
- 116 Y. Qu, Z. Li, W. Chen, Y. Lin, T. Yuan, Z. Yang, C. Zhao, J. Wang, C. Zhao, X. Wang, F. Zhou, Z. Zhuang, Y. Wu and Y. Li, *Nat. Catal.*, 2018, **1**, 781–786.
- 117 Z. Yang, B. Chen, W. Chen, Y. Qu, F. Zhou, C. Zhao, Q. Xu, Q. Zhang, X. Duan and Y. Wu, *Nat. Commun.*, 2019, **10**, 3734.
- 118 B. Wang, X. Zhu, X. Pei, W. Liu, Y. Leng, X. Yu, C. Wang, L. Hu, Q. Su, C. Wu, Y. Yao, Z. Lin and Z. Zou, *J. Am. Chem. Soc.*, 2023, **145**, 13788–13795.
- 119 J. Yang, Z. Qiu, C. Zhao, W. Wei, W. Chen, Z. Li, Y. Qu, J. Dong, J. Luo, Z. Li and Y. Wu, *Angew. Chem., Int. Ed.*, 2018, **57**, 14095–14100.
- 120 E. Zhang, T. Wang, K. Yu, J. Liu, W. Chen, A. Li, H. Rong, R. Lin, S. Ji, X. Zheng, Y. Wang, L. Zheng, C. Chen, D. Wang, J. Zhang and Y. Li, *J. Am. Chem. Soc.*, 2019, **141**, 16569–16573.
- 121 S. Wei, A. Li, J. C. Liu, Z. Li, W. Chen, Y. Gong, Q. Zhang, W. C. Cheong, Y. Wang, L. Zheng, H. Xiao, C. Chen, D. Wang, Q. Peng, L. Gu, X. Han, J. Li and Y. Li, *Nat. Nanotechnol.*, 2018, **13**, 856–861.
- 122 C. Zhao, Y. Wang, Z. Li, W. Chen, Q. Xu, D. He, D. Xi, Q. Zhang, T. Yuan, Y. Qu, J. Yang, F. Zhou, Z. Yang, X. Wang, J. Wang, J. Luo, Y. Li, H. Duan, Y. Wu and Y. Li, *Joule*, 2019, **3**, 584–594.
- 123 Y. Qu, L. Wang, Z. Li, P. Li, Q. Zhang, Y. Lin, F. Zhou, H. Wang, Z. Yang, Y. Hu, M. Zhu, X. Zhao, X. Han, C. Wang, Q. Xu, L. Gu, J. Luo, L. Zheng and Y. Wu, *Adv. Mater.*, 2019, **31**, e1904496.
- 124 H. Yang, Q. Lin, Y. Wu, G. Li, Q. Hu, X. Chai, X. Ren, Q. Zhang, J. Liu and C. He, *Nano Energy*, 2020, **70**, 104454.
- 125 C. Xia, Y. Qiu, Y. Xia, P. Zhu, G. King, X. Zhang, Z. Wu, J. Y. T. Kim, D. A. Cullen, D. Zheng, P. Li, M. Shakouri, E. Heredia, P. Cui, H. N. Alshareef, Y. Hu and H. Wang, *Nat. Chem.*, 2021, **13**, 887–894.
- 126 H. Chung, D. Cullen, D. Higgins, B. Sneed, E. Holby, K. More and P. Zelenay, *Science*, 2017, **357**, 479–484.
- 127 Y. Li, C. Chen, R. Cao, Z. Pan, H. He and K. Zhou, *Appl. Catal., B*, 2020, **268**, 118747.
- 128 U. Kramm, L. Ni and S. Wagner, *Adv. Mater.*, 2019, **31**, 1805623.
- 129 Z. Jin, P. Li, Y. Meng, Z. Fang, D. Xiao and G. Yu, *Nat. Catal.*, 2021, **4**, 615–622.
- 130 R. Chen, J. Zhao, Y. Li, Y. Cui, Y. Lu, S. Hung, S. Wang, W. Wang, G. Huo, Y. Zhao, W. Liu, J. Wang, H. Xiao, X. Li, Y. Huang and B. Liu, *J. Am. Chem. Soc.*, 2023, **145**, 20683–20691.
- 131 K. Li, W. Wang, H. Zheng, X. Wang, Z. Xie, L. Ding, S. Yu, Y. Yao and F. Zhang, *Mater. Today Phys.*, 2021, **19**, 100427.
- 132 D. Zhao, K. Yu, P. Song, W. Feng, B. Hu, W.-C. Cheong, Z. Zhuang, S. Liu, K. Sun, J. Zhang and C. Chen, *Energy Environ. Sci.*, 2022, **15**, 3795–3804.
- 133 Z. Zhang, J. Zhu, S. Chen, W. Sun and D. Wang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202215136.
- 134 H. Xiao, W. A. Goddard, 3rd, T. Cheng and Y. Liu, *Proc. Natl. Acad. Sci. U. S. A.*, 2017, **114**, 6685–6688.
- 135 C. Liu, Y. Wu, K. Sun, J. Fang, A. Huang, Y. Pan, W.-C. Cheong, Z. Zhuang, Z. Zhuang, Q. Yuan, H. L. Xin, C. Zhang, J. Zhang, H. Xiao, C. Chen and Y. Li, *Chem*, 2021, **7**, 1297–1307.
- 136 K. Sun, K. Yu, J. Fang, Z. Zhuang, X. Tan, Y. Wu, L. Zeng, Z. Zhuang, Y. Pan and C. Chen, *Adv. Mater.*, 2022, **34**, e2206478.
- 137 J. Masana, J. Xiao, H. Zhang, X. Lu, M. Qiu and Y. Yu, *Appl. Catal., B*, 2023, **323**, 122199.
- 138 Z. Chen, A. Huang, K. Yu, T. Cui, Z. Zhuang, S. Liu, J. Li, R. Tu, K. Sun, X. Tan, J. Zhang, D. Liu, Y. Zhang, P. Jiang, Y. Pan, C. Chen, Q. Peng and Y. Li, *Energy Environ. Sci.*, 2021, **14**, 3430–3437.
- 139 Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, W. Chen, K. Wu, W. C. Cheong, Y. Wang, L. Zheng, J. Luo, Y. Lin, Y. Liu, C. Liu, J. Li, Q. Lu, X. Chen, D. Wang, Q. Peng, C. Chen and Y. Li, *J. Am. Chem. Soc.*, 2018, **140**, 4218–4221.



- 140 J. R. Huang, X. F. Qiu, Z. H. Zhao, H. L. Zhu, Y. C. Liu, W. Shi, P. Q. Liao and X. M. Chen, *Angew. Chem., Int. Ed.*, 2022, **61**, e202210985.
- 141 J.-X. Peng, W. Yang, Z. Jia, L. Jiao and H.-L. Jiang, *Nano Res.*, 2022, **15**, 10063–10069.
- 142 C. Chen, Z. Chen, J. Zhong, X. Song, D. Chen, S. Liu, W. Cheong, J. Li, X. Tan, C. He, J. Zhang, D. Liu, Q. Yuan, C. Chen, Q. Peng and Y. Li, *Nano Res.*, 2023, **16**, 4211–4218.
- 143 X. Liu, Y. Liu, W. Yang, X. Feng and B. Wang, *Chemistry*, 2022, **28**, e202201471.
- 144 B. Huang, S. Huang, C. Lu, L. Li, J. Chen, T. Hu, D. Lützenkirchen-Hecht, K. Yuan, X. Zhuang and Y. Chen, *CCS Chem.*, 2022, 1–12, DOI: [10.31635/ccschem.022.202202241](https://doi.org/10.31635/ccschem.022.202202241).
- 145 N. Qiu, J. Li, H. Wang and Z. Zhang, *Sci. China Mater.*, 2022, **65**, 3302–3323.
- 146 S. Li, A. Guan, C. Yang, C. Peng, X. Lv, Y. Ji, Y. Quan, Q. Wang, L. Zhang and G. Zheng, *ACS Mater. Lett.*, 2021, **3**, 1729–1737.
- 147 W. Ren, X. Tan, W. Yang, C. Jia, S. Xu, K. Wang, S. C. Smith and C. Zhao, *Angew. Chem., Int. Ed.*, 2019, **58**, 6972–6976.
- 148 J. D. Yi, X. Gao, H. Zhou, W. Chen and Y. Wu, *Angew. Chem., Int. Ed.*, 2022, **61**, e202212329.
- 149 Y. Pan, C. Liu, N. Zhang, M. Li, M. Wang, X. Yang, H.-C. Chen, Y. Zhang, W. Hu, W. Yan, H. M. Chen, S. Liu, H. Xiao, J. Li and C. Chen, *Chem Catal.*, 2023, **3**, 100610.
- 150 Z. Liang, L. Song, M. Sun, B. Huang and Y. Du, *Nano Res.*, 2023, **16**, 8757–8764.
- 151 W. Zheng, X. Yang, Z. Li, B. Yang, Q. Zhang, L. Lei and Y. Hou, *Angew. Chem., Int. Ed.*, 2023, e202307283.
- 152 F. Li, Y. Li, Z. Wang, J. Li, D. Nam, Y. Lum, M. Luo, X. Wang, A. Ozden, S. Hung, B. Chen, Y. Wang, J. Wicks, Y. Xu, Y. Li, C. Gabardo, C. Dinh, Y. Wang, T. Zhuang, D. Sinton and E. Sargent, *Nat. Catal.*, 2020, **3**, 75–82.
- 153 Y. Zhou, F. Che, M. Liu, C. Zou, Z. Liang, P. Luna, H. Yuan, J. Li, Z. Wang, H. Xie, H. Li, P. Chen, E. Bladt, R. Quintero, T. Sham, S. Bals, J. Hofkens, D. Sinton, G. Chen and E. Sargent, *Nat. Chem.*, 2018, **10**, 974–980.
- 154 Z. Yin, J. Yu, Z. Xie, S. W. Yu, L. Zhang, T. Akauola, J. G. Chen, W. Huang, L. Qi and S. Zhang, *J. Am. Chem. Soc.*, 2022, **144**, 20931–20938.
- 155 D. L. Meng, M. D. Zhang, D. H. Si, M. J. Mao, Y. Hou, Y. B. Huang and R. Cao, *Angew. Chem., Int. Ed.*, 2021, **60**, 25485–25492.
- 156 B. Cao, F.-Z. Li and J. Gu, *ACS Catal.*, 2022, **12**, 9735–9752.
- 157 M. Wang, A. Loiudice, V. Okatenko, I. D. Sharp and R. Buonsanti, *Chem. Sci.*, 2023, **14**, 1097–1104.
- 158 L. Lin, T. Liu, J. Xiao, H. Li, P. Wei, D. Gao, B. Nan, R. Si, G. Wang and X. Bao, *Angew. Chem., Int. Ed.*, 2020, **59**, 22408–22413.
- 159 H. Deng, C. Guo, P. Shi and G. Zhao, *ChemCatChem*, 2021, **13**, 4325–4333.
- 160 T. Zhang, B. Yuan, W. Wang, J. He and X. Xiang, *Angew. Chem., Int. Ed.*, 2023, **62**, e202302096.
- 161 J. Zhang, P. Yu, C. Peng, X. Lv, Z. Liu, T. Cheng and G. Zheng, *ACS Catal.*, 2023, **13**, 7170–7177.
- 162 S. Chen, Z. Zhang, W. Jiang, S. Zhang, J. Zhu, L. Wang, H. Ou, S. Zaman, L. Tan, P. Zhu, E. Zhang, P. Jiang, Y. Su, D. Wang and Y. Li, *J. Am. Chem. Soc.*, 2022, **144**, 12807–12815.
- 163 H. Xiao, T. Cheng and W. Goddard, *J. Am. Chem. Soc.*, 2017, **139**, 130–136.
- 164 T. Cheng, H. Xiao and W. Goddard, *J. Phys. Chem. Lett.*, 2015, **6**, 4767–4773.
- 165 D. Karapinar, N. T. Huan, N. Ranjbar Sahraie, J. Li, D. Wakerley, N. Touati, S. Zanna, D. Taverna, L. H. Galvao Tizei, A. Zitolo, F. Jaouen, V. Mougel and M. Fontecave, *Angew. Chem., Int. Ed.*, 2019, **58**, 15098–15103.
- 166 X. Tan, K. Sun, Z. Zhuang, B. Hu, Y. Zhang, Q. Liu, C. He, Z. Xu, C. Chen, H. Xiao and C. Chen, *J. Am. Chem. Soc.*, 2023, **145**, 8656–8664.
- 167 X. Zhou, J. Shan, L. Chen, B. Y. Xia, T. Ling, J. Duan, Y. Jiao, Y. Zheng and S. Z. Qiao, *J. Am. Chem. Soc.*, 2022, **144**, 2079–2084.
- 168 S. Chen, B. Wang, J. Zhu, L. Wang, H. Ou, Z. Zhang, X. Liang, L. Zheng, L. Zhou, Y. Q. Su, D. Wang and Y. Li, *Nano Lett.*, 2021, **21**, 7325–7331.
- 169 J. Yin, Z. Gao, F. Wei, C. Liu, J. Gong, J. Li, W. Li, L. Xiao, G. Wang, J. Lu and L. Zhuang, *ACS Catal.*, 2022, **12**, 1004–1011.
- 170 X. Yuan, S. Chen, D. Cheng, L. Li, W. Zhu, D. Zhong, Z. J. Zhao, J. Li, T. Wang and J. Gong, *Angew. Chem., Int. Ed.*, 2021, **60**, 15344–15347.
- 171 J. Feng, L. Wu, S. Liu, L. Xu, X. Song, L. Zhang, Q. Zhu, X. Kang, X. Sun and B. Han, *J. Am. Chem. Soc.*, 2023, **145**, 9857–9866.
- 172 C. Chen, Y. Li, A. Huang, X. Liu, J. Li, Y. Zhang, Z. Chen, Z. Zhuang, Y. Wu, W. Cheong, X. Tan, K. Sun, Z. Xu, D. Liu, Z. Wang, K. Zhou and C. Chen, *J. Am. Chem. Soc.*, 2023, **145**, 21273–21283.

