



Review article

Stabilization and activation of single-atom sites for efficient CO₂ reduction in Zn-CO₂ battery

Sowmiya Palaniappan^{a,b}, Jeena Mariya Sebastian^{a,b}, Sakthivel Kaliyaperumal^a,
Padmini Moorthy^c, Balaji Ramachandran^d, Narendhar Chandrasekar^e,
Karthik Kiran Sarigamala^{a,*}

^a CO₂ Research and Green Technologies Centre, Vellore Institute of Technology, Vellore, Tamil Nadu, 632014, India

^b School of Advanced Sciences, Vellore Institute of Technology, Vellore, Tamil Nadu, 632014, India

^c Department of Electrical and Electronics Engineering, SR University, Warangal, Telangana, 506371, India

^d Department of Electronics and Communication Engineering, Koneru Lakshmaiah Education Foundation, Andhra Pradesh, 522302, India

^e Department of BioNano Technology, Gachon University, Republic of Korea

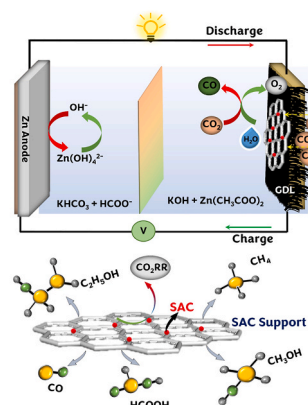


HIGHLIGHTS

- Rational design of single atom catalyst for enhanced carbon dioxide reduction.
- Controlling defects, axial ligands and metal-supports for active site stabilization.
- Selective carbon dioxide reduction through electronic tuning of single atom site.
- Optimized local coordination environment for improved catalytic activity.
- Scalable synthesis and advances in charge transfer offers durability and efficiency.

GRAPHICAL ABSTRACT

Graphical Abstract



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ABSTRACT

The fundamental challenges for zinc-carbon dioxide (Zn-CO₂) batteries lies in the sluggish kinetics of CO₂ reduction reaction (CO₂RR) that directly affects the faradaic efficiency, product selectivity, and long-term cycle life stabilization. While single-atom catalysts (SACs) have enhanced atomic-utilization and well-defined active sites, the chemistry is limited by lack of intrinsic stability-activity matching. Specifically, thermodynamic instability of isolated metal atoms leads to aggregation during electrochemical operation, and the energetic favourability of *COOH intermediate towards CO formation is constrained by a high-energy transition state, especially at the cathode-electrolyte interface. This review provides a critical perspective on making atomic-

* Corresponding author.

E-mail address: karthikkiran.sarigamala@vit.ac.in (K.K. Sarigamala).

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scale SAC engineering an intrinsic advantage for overcoming these two barriers by enabling both stabilization of single-atom sites and higher CO₂RR kinetics. The review identifies axial heteroatomic linkage engineering, along with in-plane coordination modulation and defect-mediated stabilization, as critical levers that modulate electronic structure, adsorption configuration, and reaction energetics. We discuss major unresolved mechanisms associated with interfacial charge transfer, dynamic metal-support bonding to lock in atomic diffusion suppression, and vacancy-assisted electron redistribution enabled by strong metal-support interactions. The work also highlights a mechanistic framework connecting atomic coordination descriptors with the battery performance to identify key design principles for long-lasting and kinetically viable energy storage systems.

1. Introduction

Since the industrialization, human interventions have elevated atmospheric CO₂ concentration level from ~278 ppm to ~417 ppm in the most recent census, which is escalating climate-related risks. The atmospheric CO₂ abundance together with the development of global energy demand, drives the need for carbon mitigation and grid-level renewable energy storage technologies that ensure high efficiency, environmental compatibility, and affordability [1,2]. While capturing and storing CO₂ geologically is technically feasible, the high cost and logistical hurdles often make it difficult to scale up and implement successfully. From small-scale electronics to grid-level storage, rechargeable batteries are the primary energy storage solution today. Yet, their performance parameters, such as energy density and cycle life, are highly influenced by underlying chemistry and design of the battery [3,4]. While significant progress has been made in material science, conventional energy storage systems continue to face inherent physicochemical constraints that limit their long-term cyclic stability. Beyond the technical hurdle of degradation, the environmental impact of material extraction remains a significant ethical and practical concern [5]. These challenges are driving a shift toward metal-CO₂ batteries, which use electrochemical reduction to provide a more straightforward and scalable way to produce clean energy and value-added supplemented derivatives. Of the aforementioned systems, Zn-CO₂ batteries offer particular promise due to the natural abundance and affordability of zinc, high theoretical energy density and inherent safety [6]. These batteries offer both energy storage and a conversion platform with its unique nature of coupled electrochemistry, that is, direct coupling of Zn oxidation and simultaneous cathodic CO₂ reduction, which can simultaneously produce electric power and transformation of CO₂ into value-enriched by-products during discharge.

Recently, the focus of the vast majority of existing reviews on Zn-CO₂ batteries has been on nanomaterial-level catalytic descriptors and device-level performances, whereas the practical bottlenecks that ultimately dictate cell-level viability such as slow cathodic CO₂RR kinetics, reaction intermediates and products instability, and parasitic side reactions occurring in the cathode-electrolyte interphase, received limited attention. To address these gaps, here we present a mechanistic framework for the design of stable and selective CO₂ conversion under realistic Zn-CO₂ battery operating conditions, centered around the understanding of the functionality of the single-atom catalyst (SACs). SACs are heterogeneous catalysts with individual metal atoms scattered and balanced on a supportive matrix, with no metal-metal bonds present at the active sites. By achieving nearly 100% atomic utilization, these systems develop unique electronic structures shaped by their local environment, often triggering catalytic behaviors that traditional nanoparticles simply cannot match. While atomically dispersed catalysts serve as a broad term for any metal species distributed at the atomic level, we use the term 'SAC' in this review to refer strictly to isolated, mononuclear single atoms. This distinguishes them from the broader category which might occasionally include dinuclear pairs or tiny clusters where full isolation is not guaranteed. Taking this a step further, Dual-atom catalysts (DACs) introduce pairs of metal atoms either identical or distinct stabilized in proximity by a support. Unlike classical SACs, DACs enable direct or through-support metal-metal interactions,

opening up new reaction pathways and allowing for higher metal loadings. These synergistic effects are particularly powerful for complex, multi-electron processes like CO₂ reduction, where they can significantly enhance overall performance. On the other hand, metal clusters or sub-nanoclusters consist of small aggregates of a few to tens of metal atoms, typically <2 nm, exhibiting metal-metal bonding and collective electronic properties that transition toward nanoparticle behavior. They differ fundamentally from SACs and DACs due to the presence of extended metal-metal interactions and size-dependent properties. Through both optimized atomic efficiency and specific active sites, SACs provide tunable adsorption energies for important CO₂RR intermediates, reduced kinetic barriers at the step of *COOH formation, and alleviation of competing reactions. More importantly, coordination engineering at the atomic level comprising axial heteroatomic linkages, defect-mediated stabilization, and strong metal-support interactions appear as critical, as this is a potential high-impact strategy to suppress metal aggregation, restrict atomic diffusion, and accelerate interfacial charge-transfer processes, which in turn push kinetic as well as stability barriers. This review connects atomic coordination descriptors to CO₂RR mechanisms and Zn-CO₂ battery performance metrics, identifies synthesis, stability, and electrochemical challenges central to SAC integration, and provides insight into emerging strategies aimed at robust, high-efficiency, high-metal, commercially-relevant SAC-based Zn-CO₂ energy storage systems.

1.1. Zn-CO₂ batteries: A dual-purpose platform for energy and environmental remediation

Metal-CO₂ batteries present a promising solution by merging carbon utilization with energy storage in a single system [6]. Several metal-CO₂ batteries, using active metals such as lithium, sodium, aluminium, magnesium, and zinc, have been investigated by various research groups worldwide [7]. However, their extensive application is limited due to practical issues such as the high cost of Li-CO₂ systems, which use organic electrolytes and limited product versatility in non-aqueous chemistries [8]. Whereas Zn-CO₂ batteries stand out for their use of cost-effective, water-based electrolytes and their relatively high energy density. Zinc is particularly suited for aqueous systems due to its redox potential falling within water's electrochemical stability window. A key factor here is the tendency of Zn²⁺ ions to form tight hydration complexes, a behavior that dictates much of the system's electrochemical response [9]. Even with its inherent strengths, the Zn-CO₂ battery is still held back by the slow reaction kinetics during CO₂ reduction and the discharge cycle. Overcoming these kinetic hurdles requires effective electrocatalysts that can lower activation energy and provide faster pathways for the reaction [10]. Beyond the chemistry itself, the physical makeup of the electrode including its surface architecture, porosity, and overall morphology plays a decisive role in how efficiently these catalysts actually perform. Nanostructured materials have recently shifted the landscape of CO₂ conversion, using heterogeneous catalysis to sharpen selectivity and accelerate reaction dynamics [11,12]. In these electrochemical systems, the electrode-electrolyte interface is where the real work happens. Electrocatalysis dictates how charge carriers move, directly managing the breaking and forming of molecular bonds during redox cycles. The electrochemical kinetics associated is highly sensitive

to the surface crystallography of the electrode [13,14]. Of these processes, the CO_2 reduction reaction is particularly vital for metal- CO_2 batteries, as it offers a dual benefit such as curbing carbon emissions while yielding valuable fuels and chemical feedstocks [14]. To truly optimize Zn- CO_2 performance, we need catalysts with the right physical and chemical balance to streamline gas adsorption and CO_2 RR pathways. By fine-tuning the cathode's surface atoms, particle size, and pore architecture, we can enhance mass transfer and adjust the faradaic efficiency, ultimately driving much faster reaction kinetics [15].

2. Need for a frontier catalytic material and fundamental reaction mechanisms of Zn- CO_2 batteries

Nanoparticles are often the first choice for electrocatalysis because of their high surface reactivity, but they are difficult to stabilize. Their natural tendency to gather together or aggregate rapidly shrinks the available active surface, which ultimately drags down both the efficiency and the cycling stability of the catalyst [16]. Additionally, the metal nanoparticle's intrinsic polydispersity often leads to non-uniform active sites, diminishing both reaction selectivity and overall catalytic utilization. Addressing these challenges require a multidimensional

approach, specifically by engineering better support materials and optimizing metal dispersion to prevent particle growth. A significant advancement was developed on SACs, in which individual atoms are anchored on suitable supportive materials. As illustrated in Fig. 1(a), these anchored sites undergo precise electronic structure tuning via nitrogen coordination, axial group modification, or/and defect engineering to drive the performance of rechargeable Zn- CO_2 batteries. This configuration guarantees that every atom is active, which not only sharpens selectivity but also boosts the reaction kinetics needed to make Zn- CO_2 batteries commercially viable [17,18]. Zn- CO_2 batteries have emerged as a standout platform, particularly when high-performance SAC cathodes are used to drive the selective conversion of CO_2 into valuable feedstocks [19]. By pairing a low-cost zinc anode with a sustainable aqueous electrolyte, these systems offer a practical, green alternative that is both economically and environmentally favored. However, refining the cathode with better catalyst design and electrolyte composition is the key to pushing CO_2 reduction performance even higher and maximising the total power output of these systems. Early works on Zn- CO_2 batteries was largely restricted to primary (non-rechargeable) systems, as shown in the left panel of Fig. 1(b). However, the field has since evolved toward rechargeable versions (Fig. 1(b), right

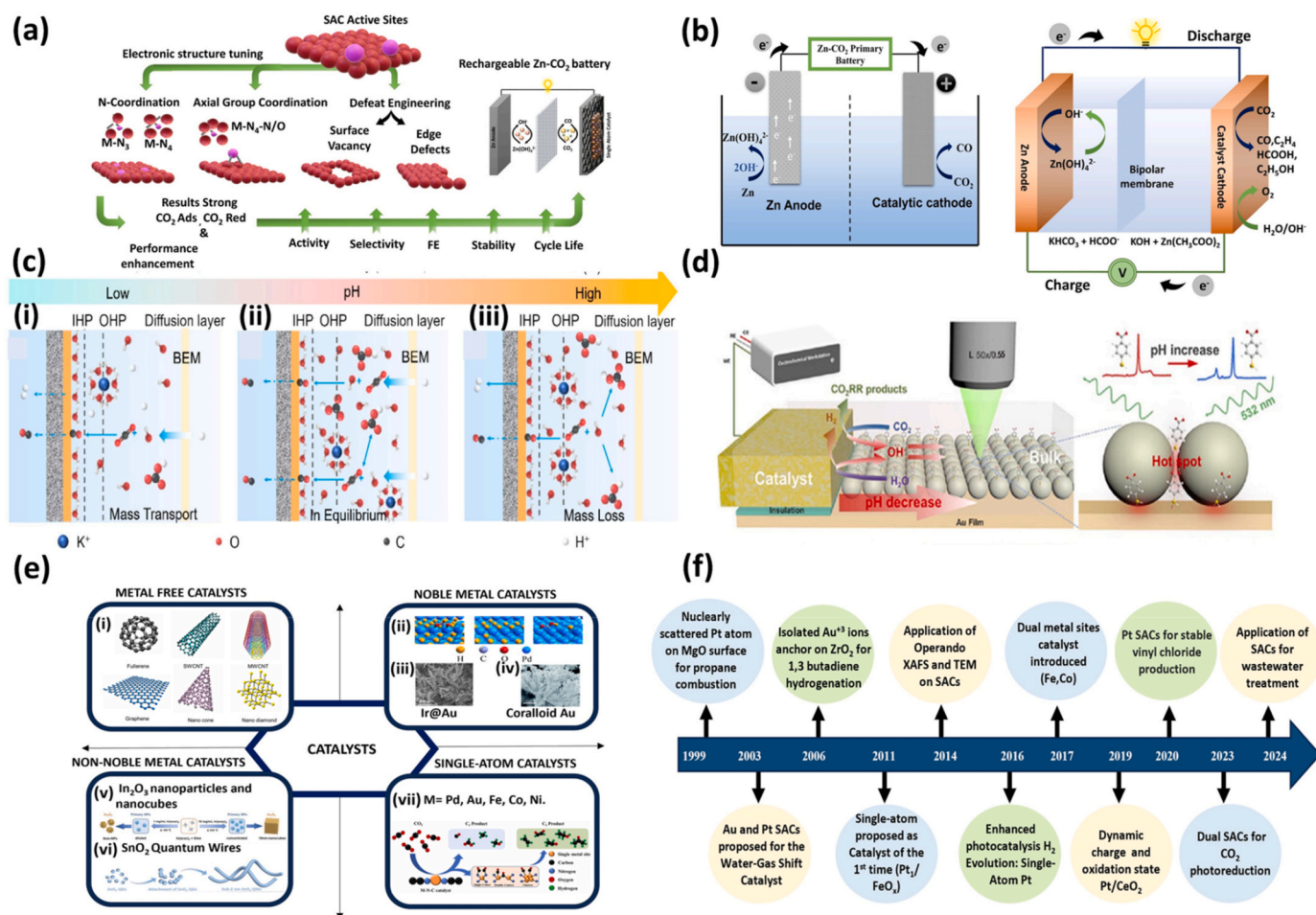


Fig. 1. (a) Schematic of SAC design strategies (electronic tuning, coordination, and defects) for enhanced CO_2 electroreduction performance. (b) Non-rechargeable and rechargeable Zn- CO_2 battery. (c) Schematic representation of (i) low, (ii) medium and (iii) high pH of the cathode-electrolyte interface. Reproduced with permission from Ref. [20] Copyright 2025, Elsevier. (d) In-situ imaging and time-resolved investigation of local pH. Reproduced with permission from Ref. [21] Copyright 2025, John Wiley and Sons. (e) Schematic representation of the type of catalysts (i) Nanocarbons. Reproduced with permission from Ref. [22] Copyright 2013, American Chemical Society. (ii) Pd nanoparticles. Reproduced with permission from Ref. [23] Copyright 2017, Springer. (iii) Ir@Au cathode Reproduced with permission from Ref. [24] Copyright 2019, John Wiley and Sons. (iv) Coraloid Au Reproduced with permission from Ref. [25] Copyright 2021, Royal Society of Chemistry. (v) In_2O_3 nanoparticles and nanocubes. Reproduced with permission from Ref. [26] Copyright 2021, John Wiley and Sons. (vi) SnO_2 Quantum wires. Reproduced with permission from Ref. [27] Copyright 2019, John Wiley and Sons. (vii) Metal-Nitrogen-Carbon (M-N-C). Reproduced with permission from Ref. [28] Copyright 2023, Elsevier. (f) Progression of Single-atom catalysts over time [29–40].

panel), which have progressed from selectively yielding carbon monoxide (CO) to generating even more sophisticated, high-value products a trend that continues to push the boundaries of what these aqueous systems can achieve. To provide a systematic overview, we examine the core working mechanisms of Zn-CO₂ batteries and the pivotal role SACs play in driving CO₂ electroreduction. From there, we explore the intrinsic challenges of both catalyst design and battery performance, offering a critical look at the real-world obstacles in synthesis, practical deployment, and scaling these systems for industrial use.

2.1. Mechanisms of CO₂ reduction in primary Zn-CO₂ cells

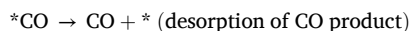
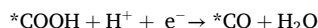
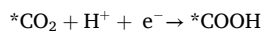
In a primary Zn-CO₂ setup, the battery operates fundamentally in discharge mode, relying on a zinc anode, a liquid electrolyte, and a catalyst-coated cathode to function. These systems are defined by their irreversible electrochemical pathways, meaning the materials are consumed in a single cycle [41]. As the battery runs, the zinc anode oxidation provides the necessary drive for the CO₂RR at the cathode interface [42]. The first reported example of such a battery was presented by Peng et al., in 2019, implementing Cu₃P/C nanocomposite catalyst for CO₂ reduction to CO. This system achieved an open-circuit voltage (OCV) of 1.5 V and a faradaic efficiency (FE) (fraction of charge contributing to the desired CO₂ conversion) of 47% [43]. In most heterogeneous catalytic systems, CO₂ reduction begins with its adsorption onto the metal catalyst surface, typically proceeding through a two-electron, two-proton transfer mechanism. Reduction process of CO₂ at the compartment of the cathode generally follows two major pathways [41].

(a) Concerted proton-electron transfer (CPET) pathway

In the CPET, the CO₂ molecule attached to the catalyst surface leads to *COOH intermediate. At the end of the reaction process, *CO and H₂O are released by taking the second proton and electron.

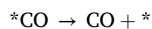
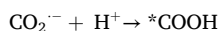
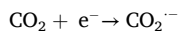
(*) Active sites on the catalyst surface where intermediates adsorb

CO₂ + * → *CO₂ (adsorption onto the catalyst surface)

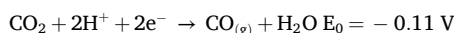


(b) Decoupled electron and proton transfer (DPET) pathway

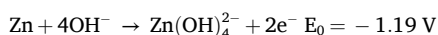
In DEPT, the initial step differs from the formation of the carbon dioxide radical anion (CO₂•⁻), which is followed by the addition of one proton to form the *COOH intermediate. The DEPT pathway was unfavorable because it requires a high negative potential (−1.9 V vs reversible hydrogen electrode) (RHE). The rate and specificity of the CO₂ reduction are controlled by the binding energies of the intermediate species.



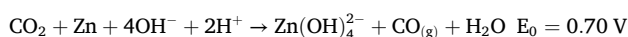
Cathodic reaction:



Anodic reaction:



Overall discharge reaction:

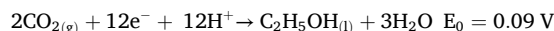
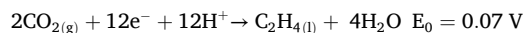
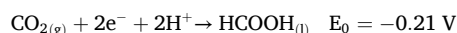
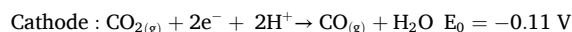
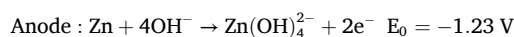


While primary Zn-CO₂ batteries provide a simple means of CO₂ electrochemical conversion, their discharge-only nature limits their practical applications.

2.2. Operational mechanism in rechargeable systems

Rechargeable Zn-CO₂ systems are gaining attention because they can cycle through both charge and discharge, allowing for truly reversible CO₂ conversion. Most of these batteries use a dual-chamber setup, physically divided by an ion-exchange membrane. In this configuration, the cathode sits in a neutral aqueous electrolyte, typically KHCO₃ with an added buffer, while the zinc anode is submerged in an alkaline mix of KOH and zinc acetate [44]. This separation is crucial because it acts as a barrier against parasitic side reactions that would otherwise impede the CO₂ reduction process. By managing both electron and proton transfer during conversion, these rechargeable designs also open the door to a much broader variety of reduction products. The redox reactions governing the system are as follows:

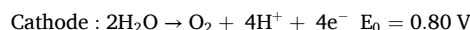
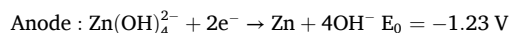
Discharging mechanism:



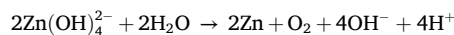
Overall discharge reaction:



Charging Mechanism:



Overall charge reaction:



By carefully controlling the applied potential, electrolyte composition, and catalyst properties, rechargeable Zn-CO₂ batteries can selectively generate different carbon-based products, including CO, HCOOH,

Table 1

The primary CO₂RR products and their corresponding reduction potentials under neutral conditions are summarized below [45].

S. No	Product	Electron transfer number	Reaction	Reduction potential [E ₀ vs RHE]
1	CO	2	CO _{2(g)} + 2e ⁻ + 2H ⁺ → CO _(g) + H ₂ O	−0.11
2	HCOOH	2	CO _{2(g)} + 2e ⁻ + 2H ⁺ → HCOOH _(l)	−0.21
3	CH ₃ OH	6	CO _{2(g)} + 6e ⁻ + 6H ⁺ → CH ₃ OH _(l) + H ₂ O	0.03
4	CH ₄	8	CO _{2(g)} + 8e ⁻ + 8H ⁺ → CH _{4(g)} + 4H ₂ O	0.17
5	CH ₃ COOH	8	2CO _{2(g)} + 8e ⁻ + 8H ⁺ → CH ₃ COOH _(l) + 2H ₂ O	−0.26
6	C ₂ H ₅ OH	12	2CO _{2(g)} + 12e ⁻ + 12H ⁺ → C ₂ H ₅ OH _(l) + 3H ₂ O	0.09
7	C ₂ H ₄	12	2CO _{2(g)} + 12e ⁻ + 12H ⁺ → C ₂ H _{4(l)} + 4H ₂ O	0.07

CH₃OH, CH₄, CH₃COOH, C₂H₄, and C₂H₅OH. The specific reduction products and their underlying reaction mechanisms are given in Table 1, providing a side-by-side comparison of how these pathways proceeds CO₂RR.

In Zn-CO₂ batteries, a favourable discharge potential ensures spontaneity, but efficient charging is critically dependent on catalyst innovations that can fine-tune the cathode-electrolyte interface. The goal here is to optimize double-layer formation and the way CO₂ reduction intermediates anchor to the surface. Fig. 1(c) illustrates how electrolyte pH dictates the interfacial structure and the movement of ions across the inner Helmholtz plane (IHP), outer Helmholtz plane (OHP), and the broader diffusion layer. When the pH is low (Fig. 1(c(i))), protons are abundant, and mass transport is largely driven by H⁺ ions moving inward, which streamlines proton-coupled electron transfer. At a more neutral pH (Fig. 1(c(ii))), the system finds a middle ground, a dynamic balance between proton consumption and OH⁻ generation creates a steady ionic flow and a more stable environment at the electrode. On the far end of the scale at high pH (Fig. 1(c(iii))) the buildup of OH⁻ near the surface starves the reaction of protons. This leads to severe mass transport bottlenecks often called “mass loss” where the sluggish arrival of reactants or the slow removal of products essentially inhibits the reaction kinetics [20]. Ultimately, these local shifts in pH and interfacial layout decide the intermediate mechanisms, how the double layer forms, and how efficiently the Zn-CO₂ system can actually convert CO₂.

While aqueous rechargeable Zn-CO₂ batteries hold immense potential, several technical hurdles still block their path to widespread use. To clear these obstacles, we need a clearer window into what is actually happening at the electrode surface. In-situ spectroscopic studies represent a transformative approach by recording potential-dependent spectra in real-time, they allow us to track the exact moment surface-bound species appear, shift, or vanish. Techniques like in situ Raman or FTIR spectroscopy offer the direct evidence needed to map these interfacial processes, while environmental transmission electron microscopy (ETEM) lets us actually visualize the catalyst in action under realistic working conditions [46–48]. Additionally, Fig. 1(d) highlights a time-resolved, in situ strategy designed to probe how local pH evolves right at the catalyst-electrolyte interface during CO₂RR. By employing a confocal optical setup, we can monitor spatial pH fluctuations directly above the catalyst surface in this case, deposited on an Au film giving us a high-resolution map of the chemical environment as the reaction unfolds. As CO₂RR proceeds, the consumption of protons and the simultaneous buildup of OH⁻ ions cause the local alkalinity to spike near the active sites, even as the bulk electrolyte stays relatively neutral. This creates a sharp pH gradient that stretches from the catalyst surface out into the diffusion layer. Beyond this global shift, localized regions of elevated pH develop at specific catalytic sites, providing clear evidence of spatial heterogeneity across the electrode surface [21]. Such in situ visualisation highlights that the reaction environment at the interface deviates substantially from bulk conditions and plays a critical function in determining reaction mechanisms, intermediate stabilization, and product selectivity. These interfacial issues become even more problematic when the catalyst is inefficient at converting CO₂. This limitation arises due to the inherent chemical inertness of CO₂ molecules, which requires high activation energy for reduction and competes with HER in aqueous electrolytes, thereby reducing the generation of selective CO₂ reduction by-products. Beyond the challenges of conversion, electrolyte stability remains a significant bottleneck in the advancement of Zn-CO₂ systems. The highly alkaline environment required at the Zn anode frequently triggers parasitic side reactions and the irreversible accumulation of carbonates both of which markedly degrade cell performance and cycle life. Overcoming these interfacial roadblocks necessitates the development of high-efficiency electrocatalysts. Specifically, these materials must demonstrate a superior ability to sharpen CO₂ reduction selectivity while effectively suppressing the thermodynamically favourable, yet parasitic, hydrogen evolution reaction (HER) [44].

2.3. Advancements in electrocatalysts for rechargeable Zn-CO₂ batteries

The operational success of Zn-CO₂ batteries is entirely dictated by the efficiency and selectivity of the cathode electrocatalyst. Consequently, recent efforts have shifted toward sophisticated material engineering and surface modifications to push the boundaries of catalyst design. Because CO₂ is a fully oxidized species with carbon in its highest +4 oxidation state, converting it into energy-dense products requires a massive, coordinated electron transfer. Electrocatalysts are essential here, not merely to lower the activation energy barrier, but to provide the specific pathways necessary for this reduction to occur [49]. Beyond just accelerating the reaction, the cathode catalyst acts as the primary governor of the system's kinetics, product distribution, and overall voltage efficiency. Subtle shifts in the chemical composition or electronic structure of these materials have profound effects on the battery's underlying mechanism, its power density, and its long-term cycling stability. Currently, the landscape of cathode catalysts for Zn-CO₂ systems is divided into four primary architectures like metal-free, noble metal, non-noble metal, and SACs, as categorized in Fig. 1(e) [50]. Carbonaceous materials are the primary non-metallic catalysts (Fig. 1(e(i))) due to their high chemical inertness, larger specific area, good electrical conductivity, and simple structural modification. They are available in various forms, including graphene and carbonized material derivatives containing hetero atoms [22]. Pure carbon materials are inert to CO₂RR, as they have only unipolar, slightly polarizable carbon atoms to chemisorb and catalyze CO₂ molecules. The electronic configuration of carbonaceous materials is optimized via heteroatom dopants, including nitrogen, boron, and phosphorus, into the carbon lattice and by the creation of intrinsic carbon defects, which serve as catalytically active sites. It is empirically and theoretically validated that heteroatom doping enhances adsorption enthalpies, minimizes the energy barrier for CO₂RR activation, and fast-tracks the chemisorption of key intermediate (*COOH) in proximity to these active centers [50]. Wang et al. synthesized the initial model of a metal-free catalyst with nitrogen-functionalized graphene for the production of formate by CO₂ reduction [19].

Conventional noble metal catalysts, such as Pd, Ag, Au, and non-noble metal catalysts, exhibit higher catalytic activity for CO₂ reduction. Fig. 1(e(ii-iv)) displays some of the noble metal catalysts, such as Pd nanoparticles, Ir@Au, and Coraloid Au, which are used in Zn-CO₂ batteries [23–25]. Many non-noble metals, originating from both d-block transition metals and p-block metals have also been investigated actively for CO₂ reduction. Fig. 1(e(v and vi)) shows p-block metal oxides, such as In₂O₃ nanoparticles and SnO₂ Quantum wires, which are used as cathodes for CO₂RR [26,27]. However, their widespread application is stalled by lower atom utilization, aggregation, and limited long-term stability, making large-scale implementation challenging. Alternatively, single atom-based catalysts are emerging as efficient electrocatalysis, where isolated metal atoms are dispersed on a suitable support matrix. Fig. 1(e(vii)) shows the arrangement of a single metal atom coordinating with nitrogen and carbon support, which is collectively known as a metal-nitrogen-carbon (M-N-C) complex, involved in CO₂ reduction. The unique structural features with high atomic utilization and tunable electronic properties enhance reaction kinetics while maintaining a lower quantity and excellent selectivity for CO₂ reduction [28]. Beyond simply boosting catalytic performance, these materials provide a commercially feasible pathway for scaling CO₂ reduction technologies. The evolutionary timeline of SACs has been one of rapid and sophisticated advancement transforming from the early, fundamental concept of the isolated atom into the rationally designed, precision architectures currently in use.

3. Evolution progress-property correlations in SACs for Zn-CO₂ battery

Among the heterogeneous catalysts, noble metals have found wide

applications in petrochemical reactions, pharmaceutical drug synthesis, and environmental protection. But the high cost and limited supply are serious obstacles, and thus novel strategies to improve catalytic efficiency with decreased material consumption are of great importance [51]. To address such shortcomings, a shift from nanoclusters to single isolated multiple-atom site SACs is being developed as an effective strategy to achieve maximum use of the metal atom, while retaining catalytic activity. In comparison with the traditional nanoparticle catalysts, SAC will allow every metal atom to be in contact with reactants, which could effectively make use of active sites [52]. SACs have unique features that are different from those of nanoparticle catalysts and molecular metal complexes. The extraordinary selectivity, catalytic performance and stability of the supported monometallic catalysts in oxidation, hydrogenation and water-gas shift (WGS) reactions have been attributed to their low-coordination environment, strong metal-support interactions, and high atomic efficiency. The initial investigations were mainly dedicated to noble-metal-based SACs supported on metal oxides. Nevertheless, with the development of synthetic means and elaborate computational models such as in situ characterizations, one can introduce non-noble metals made within various supportive matrices like designed carbon structures, metal-organic frameworks (MOFs) or 2D materials [53,54]. The homogeneity of SAC's active sites enables accurate structure-functional correlation investigations and improves computational modelling accuracy, which is a significant benefit over traditional nanoparticle catalysts. SACs can achieve ~100% active site exposure because of their special design, which also preserves the chemical and thermal stability of the heterogeneous catalyst [55]. Fig. 1 (f) shows the development of SACs emerging from the framework of heterogeneous catalysts. In the early stages of SAC research, minor attention was given to tailoring coordination environments, and their initial success was largely incidental, driven by the necessity of maintaining low metal content. However, as the field evolved, researchers recognized the importance of designing well-defined metal-support interactions, leading to the enlargement of SACs with high thermal stability and exceptional catalytic activity, particularly in selective hydrogenation reactions [29–40]. Before the official invention of the phrase “single-atom catalyst”, several research teams had already published reports on “atomically dispersed”, “isolated atom”, which were catalytic metal atoms stabilized on oxide supportive matrix. SACs have become a paradigm shift material in the catalysis field due to their unique features, including the ability to overcome the shortcomings of conventional heterogeneous catalysts but still holding the advantages of homogeneous catalysts, and drastically decreasing noble metal usage.

We have also observed that SACs play active roles in lowering overpotentials, which would lead to superior overall charge-discharge performances and energy efficiencies for Zn-CO₂ batteries. In addition, these materials are inexpensive to produce because a relatively small quantity of metals is employed (e.g., Pt, Co and Fe), which minimizes materials expense compared to catalytic outputs. SACs act as a promising catalyst for carbon-neutral energy storage by the adsorption of atmospheric waste CO₂ and convert it into valuable chemical products [56–58]. This study entirely focuses on the active sites, which control and direct the selectivity of products (eg., CO vs. formate) as well as their reaction pathway. Pt₁/FeO_x was the first single-atom catalyst employed for CO oxidation with superior stability. The presence of empty d-orbitals and a positive charge in the Pt atom constructs an interaction with the oxygen of FeO_x support. Due to the strong attraction of electrons towards FeO_x, the Pt atom anchors single and stable to its surface [59]. Especially for CO₂ reduction, Li et al. synthesized N- and O-coordinated single-atom Pd catalysts, named Pd₁-N-CB and Pd₁-O-CB, and their work showed that asymmetric oxygen atom coordination could greatly improve the CO₂RR selectivity with 99.6% FeCO. This is further confirmed by the theoretical calculation, which indicates a lower free energy of Pd₁-O-CB due to the presence of an electronegative oxygen atom. While Pd₁-O-CB employed as a cathode material, it provides a power density of 1.72 mW cm⁻² and maintains durable production of

CO for over 100 h [60]. Some of the fundamental, catalytic, and tunable properties of SACs are discussed in the sections below, which make this catalyst arena a robust platform for next-generation Zn-CO₂ energy storage technologies.

3.1. Unique electronic structure and catalytic properties

The examination of the interface between the metal surface and the reactant species is highly needed to understand the reaction kinetics. Fig. 2(a) shows the adsorption of one atom on a neighbour site, which drives CO₂ electrochemical reduction. The CO₂ molecules adsorb on the metal center after occurring activation via electron transfer, and are then decomposed into CO via reduction, followed by desorption from the catalyst surface. The core metal center coordinates with the surrounding atoms, which determines the coordination environment and geometric structures of active sites that are essential for stabilizing reaction intermediates for CO to be produced. The catalytic efficiency of heterogeneous catalysts is highly dependent on the surface-to-volume proportion of their active sites. This suggests that smaller particle sizes typically correspond to greater activity per atom, as shown in Fig. 2(b). The logical extreme of this downsizing effort is SACs, where separate metal atoms are anchored individually onto the supportive matrix [61]. Wang et al. concluded that distinct geometric and electronic configurations of 2D materials and the single atom have a mutually beneficial relationship in enhancing the catalytic activity. The 2D materials have a homogeneous, regular planar structure that enables precise geometric regulation with the coordinated metal atom. Single atoms imprinted within the lattice of 2D materials can alter their configuration and activate the catalytically inactive site by initiating the catalytic properties of the 2D lattice [66]. The catalytic efficacy of a single metal atom is influenced when it interacts with its substrate. This interaction involves properties such as electronic structure and spatial coordination.

In particular, the local atomic environment around the single atom as shown in Fig. 2(c) represents the central metal atom, which acts as a major active site for catalysis. The first shell (heteroatoms such as nitrogen or carbon) represents the neighbouring atoms bonded to the core metal atom. Notably, these first-shell atoms affect the electronic coordination of the core metal atom. The second shell atoms are more distant from the central metal atom and provide long-range electronic interactions, which enhance adsorption and activation of any transient species involved in catalysis. The distance between two central atoms (d_{int}) is key to differentiating isolated SACs from nano-clustered catalysts. Moreover, vital active sites are described as central metal mediator with adjacent co-ordinated atoms [59]. The stability of SACs against sintering and aggregation during operation is governed by two key mechanisms: thermodynamic stability and kinetic stability. These mechanisms are clearly illustrated in the free-energy diagram shown in Fig. 2(d). In this schematic, the x-axis represents the reaction coordinate progressing from aggregated nanoparticles through a transition state to isolated single atoms dispersed on the support, with the reverse direction corresponding to the dispersion process, and the y-axis denotes Gibbs free energy.

Thermodynamic stability indicated by the green curve in Fig. 2(d) shows the transition from nanoparticles to an isolated single atom by the negative free energy ($\Delta G < 0$). This favours the lower free energy for a single atom than the clustered nanoparticles and makes the dispersion process spontaneous. E_d (downward arrow) represents the inherent energetic preference for an isolated atomic configuration, and it is realised through efficient metal-support interactions on defect-rich carbon support. In contrast, the black curve in Fig. 2(d) indicates the kinetic stability that occurs in positive free energy ($\Delta G > 0$). This denotes that the nanoparticle state is thermodynamically more stable. However, a high activation energy barrier (E_a) represents the peak along the aggregation pathway, effectively trapping the metal atom, preventing its coalescence. When the E_a is high, it immobilizes the single atoms in a metastable isolated state, even though aggregation is

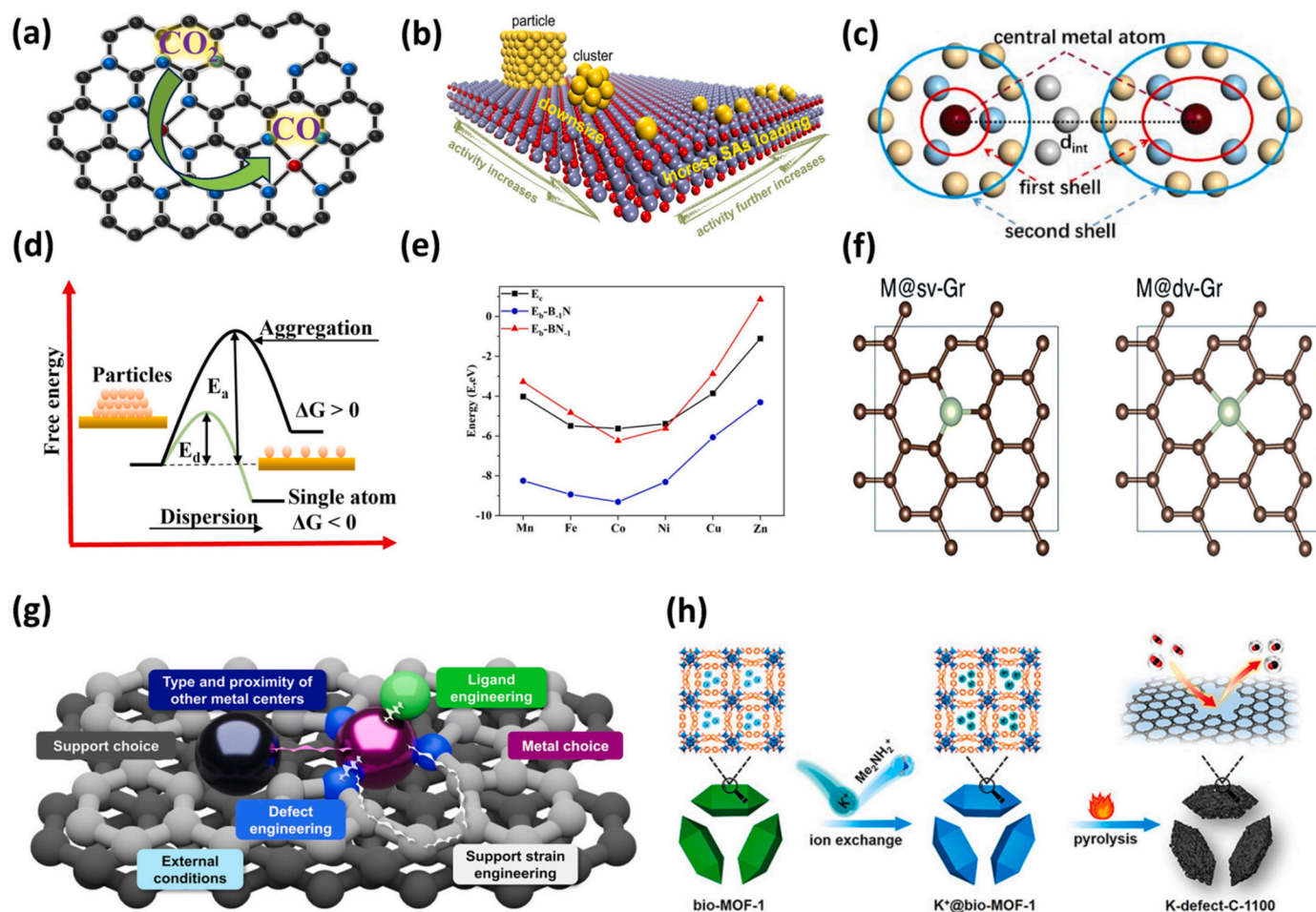


Fig. 2. (a) Catalytic role of SAC in CO₂ reduction. (b) Catalytic activity: an initial increase achieved by downsizing the active component, followed by a rise with greater single-atom (SA) loading. Reproduced with permission from Ref. [61] Copyright 2023, Elsevier. (c) The diagram illustrates a central single metal atom and its surroundings. Reproduced with permission from Ref. [59] Copyright 2021, American Chemical Society. (d) Free energy diagram of SAC (E_a-energy aggregation and E_d-energy dispersion). (e) Binding energy and cohesive energy in TM@B₁N and TM@BN₁. Reproduced with permission from Ref. [62] Copyright 2025, Multi-disciplinary Digital Publishing Institute. Top view of (f) M@sv-Gr and M@dv-Gr. Reproduced with permission from Ref. [63] Copyright 2017, Royal Society of Chemistry. (g) Overview of synthetic and operational strategies of SACs. Reproduced with permission from Ref. [64] Copyright 2023, American Chemical Society. (h) K-defect-C-1100 preparation process. Reproduced with permission from Ref. [65] Copyright 2022, John Wiley and Sons.

energetically downhill in the reverse direction. This kinetic barrier is essential for a stable Zn-CO₂ system, especially during the adsorption of reaction intermediates and constant cycling, where it prevents the migration of a single atom into clusters. Hence, thermodynamic stability is driven by the lower free energy of a dispersed single atom, and kinetic stability is governed by a substantial energy barrier that impedes atomic rearrangement and agglomeration. Both mechanisms contribute to the overall durability of SACs under operational conditions [67,68]. For example, Yu et al. and their co-worker discussed single-atom transition metal dispersion on defective hexagonal boron nitride with different vacancies (B and N) using binding energy (E_b), Cohesive energy (E_c), Formation energy (E_f), and dissolution potential (U_{diss}). The thermodynamic studies reveal that the single atom satisfies E_f < 0 and U_{diss} > 0, demonstrating both practical viability and electrochemical stability. The E_b measures the adhesion strength between the central metal atom and the support, E_c quantifies the metal atom's tendency toward cluster formation.

$$E_b = E_{\text{total}} - E_{\text{def}} - E_M$$

$$E_c = E_{\text{bulk}} - E_M$$

Here, E_{total}, E_{def}, E_M, and E_{bulk} represent the total energy of the metal-anchored system, defective support, individual metal atom, and bulk

metal per atom. Higher negative E_b and E_c values signify stronger metal-support adhesion and aggregation tendencies. Fig. 2(e) depicts E_b < E_c < 0, which favours metal-support bonding over metal-metal clustering, validating single-atom stability. In B-vacancy sites, all transition metals satisfy E_b < E_c, ensuring better anchoring capability. But in contrast, only Co and Ni satisfy E_b < E_c at N-vacancy sites, and other transition metals, Fe, Zn, Cu, and Mn, show E_b > E_c, indicating aggregation formation. Similarly, Back et al. identified the optimal transition metal-graphene configuration by the binding energies of 12 transition metals (Ag, Au, Ir, Pd, Pt, Rh, Ru, Co, Fe, Ni, Os) on graphene with single (M@sv-Gr) or double vacancies (M@dv-Gr) as shown in Fig. 2(f) using a 24-C supercell (15 Å vacuum). For electrochemical free energy profiles in CO₂ reduction, the computational hydrogen electrode method (CHE) was used with limiting potentials determined as U_L = -ΔG_{MAX}/e. Free energies incorporated Zero-point energy (ZPE), enthalpy, entropy corrections (298.15 K), and solvation stabilization (*COOH: -0.25 eV, *CO: -0.1 eV, *OH: -0.5 eV) [62,63]. The binding energy of metal monatoms on nitrogen-doped graphene supports with different coordination environments (Fe, Co, Ni, Cu; 28 models in total) is analyzed to assess the kinetic stability of the single-atom catalysts. The E_b values for M-N_x-C_{3-x} and M-N_x-C_{4-x} structures are predominantly negative, indicating that metal anchoring to the N-doped carbon matrix is thermodynamically favourable and the desorption or migration of the metal atom is

kinetically hindered. Negative E_b in the configuration of $M-N_x-C_{4-x}$ compared with $M-N_x-C_{3-x}$ implies the presence of higher nitrogen coordination increases the kinetic barrier for atomic diffusion and improves the kinetic stability. For most metal centers when the nitrogen coordination is 2, $M-N_x-C_{4-x}$ is more stable than $M-N_x-C_{3-x}$, and when the nitrogen coordination is 1, $M-N_x-C_{3-x}$ is more stable than $M-N_x-C_{4-x}$. Among all the metals, Ni-N-C shows the lowest binding energies (more negative), suggesting Ni monatoms are kinetically more stable and least prone to leaching under reaction conditions [69]. These thermodynamic stability conditions, $E_f < 0$, $U_{diss} > 0$, and $E_b < E_c$, ensure structural and electrochemical stability with kinetic stability that is reflected in large diffusion barriers and strong anchoring, effectively inhibit metal aggregation, and maintain the maximum density of well-dispersed active sites. Such thermodynamically and kinetically robust single-atom centers provide a stable platform for fine-tuning the adsorption energetics of intermediates such as $^*COOH$ and $^*CO$, which lowers the overall reaction free energy barriers and enhances selectivity, catalytic efficiency, and long-term durability in CO_2 reduction systems. Hence, strategies were induced in the coordination environment for accommodating a single atom as well as reducing the activation energy barrier for key intermediates.

3.1.1. Strategies for tuning electronic features of SACs

The SAC design starts with the selection of an appropriate host for our use. By carefully tuning the exact speciation and coordination of the coordinating atom, we are able to coarse the electronic properties of the metal site. This occurs through interaction at (i) anchoring sites in the matrix, (ii) exchangeable ligands and (iii) neighbouring metal atoms or defects. Furthermore, control will be applied to extrinsic parameters such as the induced electromagnetic field or external bias, allowing for an increased performance in tuning the electronic structure of SACs [64, 70], which has been demonstrated in Fig. 2(g). As a result, much effort has been dedicated to host engineering of the matrix in the process for immobilizing metal atoms as SACs. Defect sites, such as vacancies or heteroatoms, of the host trap each metal atom via covalent or ionic interaction. For instance, Fig. 2(h) refers to an increase in heteroatom doping, leading to heavy intrinsic carbon defects facilitating spread out charge thus activating the carbon atoms on these defect sites for enhanced catalytic activity. Ling et al. synthesized a high defect porous carbon (K-defect-C-1100) by a K^+ -assisted strategy and have 12-vacancy-type defects [65]. While defect engineering has shown promise in tuning catalytic performance, accurately assessing its effect on the metal center's orbital configuration remains challenging due to characterization and computational method limitations. Effective stabilization and adaptable bonding of metal centers, optimized for specific catalytic cycles, requires careful optimization of the anchoring sites on the host.

We also observed that the supporting strain-induced modification offers a different strategy to control active site configuration by adjusting the bond lengths between central metal atoms and surrounding ligand atoms. For example, in Ag-SACs, holdup on microporous Mn-hollandite used for oxidation of formaldehyde, varying synthetic methods such as *anti*-Ostwald ripening and wet impregnation resulted in different interatomic distances in the Ag-O and Ag-Ag near-neighbour shells. The stronger electronic metal and support interaction achieved through *anti*-Ostwald ripening resulted in a rise in the energy levels of Ag d-orbital states. This shift facilitated O_2 activation by enhancing the density of states of its antibonding π^* orbital and/or decreasing the population of its π - and 5σ -bonding orbitals [65]. This implies the presence of local strain, induced by the synthetic approach, although not explicitly stated. Ligand manipulation in SACs also provides a promising way to fine-tune catalytic activity by changing the chemical environment of single isolated metal atom [71].

Nevertheless, by modifying the positions of such ligands, one can tune the coordination environment of the metal and its capability to react with substrates as well as alter its catalytic properties. Therefore, proper ligand design is an important tool for modern catalysts with an

advanced property. Introduction of a second metal atom into the coordination sphere will be an apt way to design such a modern catalyst. This strategy changes the electronic charge surrounding of the active metal-core. For example, alkali metals are well known for electron density donation, leading to an effective modulation on the catalytic activity [72,73]. However, a more recent and increasingly prominent strategy involves the combination of a second transition metal atom, creating a bimetallic single-atom system. This integration often results in synergistic catalytic effects that are unattainable with single-metal SACs [74]. The proximity and type of the second metal atom significantly influence the electronic interactions and orbital hybridization with the primary metal. All the above strategies including heteroatom doping, strain-induction, ligand modification, and bimetallic incorporation are interconnected methods which can alter the d-band center and charge state of the active sites SACs. The heteroatom doping and bimetallic system adjusts charge transfer and incorporates a synergic effect, whereas strain and ligand engineering modify bond length and coordination sphere [75,76]. Therefore, by focusing on the strategic incorporation of the heteroatom doping, both strain induction and ligand engineering can be controlled at the atomic level. In the bimetallic concept, the second metal can induce strain on the primary metal and also can act as a ligand modifier. However, beyond various strategies, it is essential to understand the intrinsic function of SAC in CO_2 reduction.

3.2. Role of SACs in facilitating CO_2 reduction pathway

SACs possess distinct catalytic features owing to the atomically isolated active centers, which usually result in the selective production of C_1 products during CO_2RR . The C_1 products are CO, CH_3OH , $HCOOH$ and CH_4 as presented in Fig. 3(a-d) [77]. This kind of selectivity can be deduced from isolated properties of the active centers in SACs, which prohibit the coupling between reaction intermediates. This coupling is also required for C_{2+} products (multi-carbon products such as C_2H_4 , C_2H_5OH and acetone, which are produced through C-C coupling). Therefore, SACs primarily catalyze CO_2 conversion to single carbon products including CO, $HCOOH$, CH_4 and CH_3OH (or indeed its conjugate base, formate). By systematically investigating the elementary pathways of the formation for these important small C_1 products, we expect the mechanistic features of CO_2 activation, electron/proton transfer and intermediate stabilization to regulate product selectivity concerning SAC-based CO_2RR . Moreover, since the production of multiple carbons is difficult to achieve in SACs owing to a limited number of single atomic active sites, we also briefly introduce feasible C-C coupling pathways for the formation of C_{2+} products.

The electrochemical reduction of CO_2 to CO is a well-established reaction pathway and the generation of the $^*COOH$ intermediate is generally considered as a critical step. For SACs, the moderate adsorption energy of $^*COOH$ on individual active sites announces a high-selectivity toward CO as product of CO_2RR . Selective production of CO is very important because they have industrial interest in the Fischer-Tropsch process and WGS reaction, as CO is a key raw material for the production of synthesis gas and hydrocarbons. The mechanism usually initiates with the CO_2 adsorption on the surface, then a CPET process will produce an intermediate $^*COOH$. This intermediate is then the site of a second 'CPET' step, in which $^*COOH$ is reduced to $^*CO$ and a water molecule evolves. At last, the weakly adsorbed $^*CO$ desorbs from the catalyst surface, producing CO. Alternatively, the $^*COOH$ may participate in a single-electron reduction of CO_2 to yield the intermediacy of $^*CO_2^-$. This is succeeded by a proton-unaccompanied process of electron transfer. In this mechanism, there is the first step of protonation where a proton produced by autoionization of water associates with $^*CO_2^-$ to produce $^*COOH$. This other pathway emphasized the role of electron transfer and availability of protons that control reaction kinetics [80]. The rate-determining step (RDS) in CO_2RR is further discussed by Tafel slope analysis. The Tafel slope gives us some information about the relation between overpotential and partial

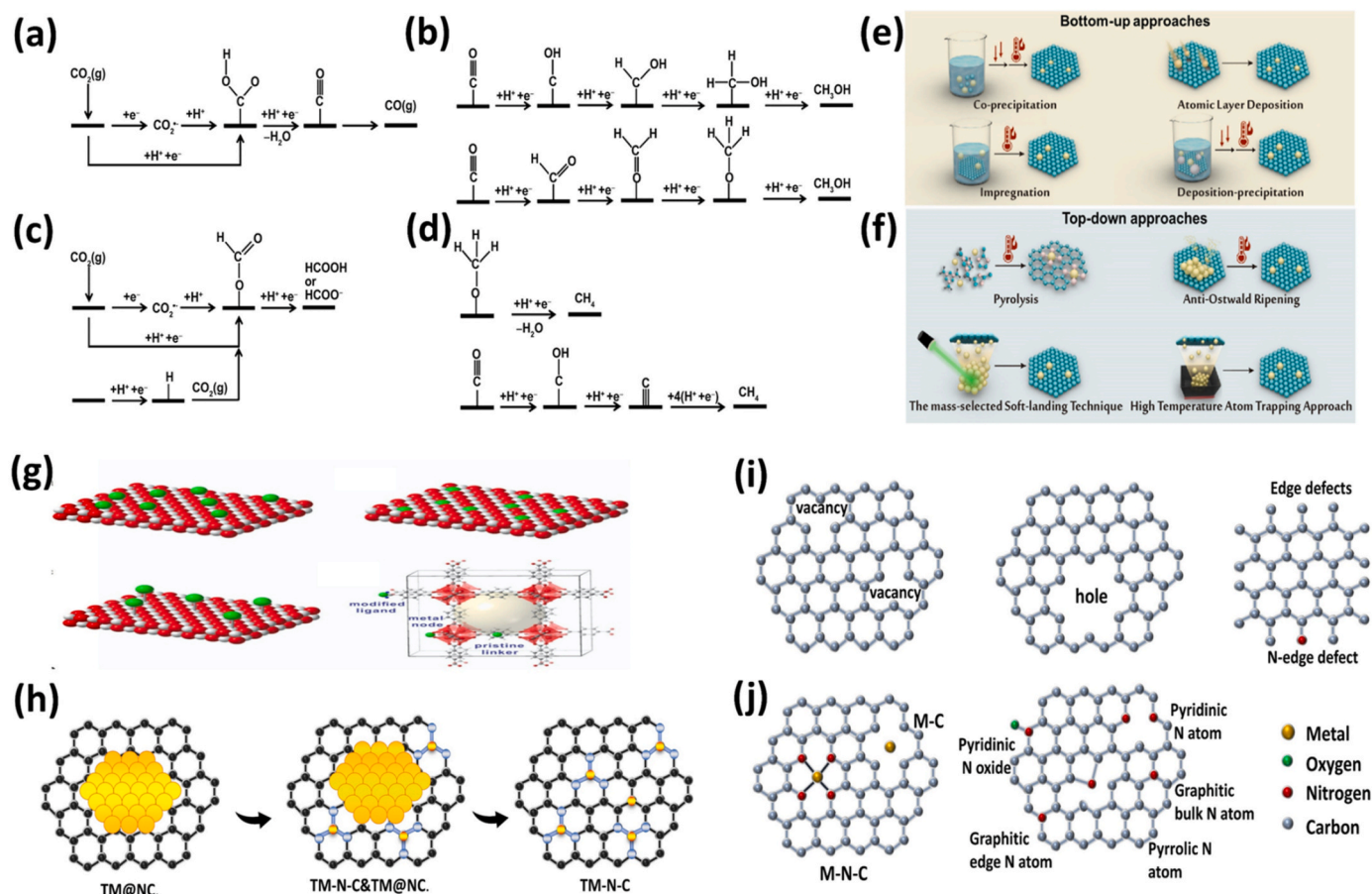


Fig. 3. Possible reaction mechanism of CO₂RR for the products (a) carbon monoxide, (b) methanol, (c) formic acid or formate, (d) methane. Reproduced with permission from Ref. [77] Copyright 2022, Elsevier. (e-f) Schematic illustration of single-atom catalysts synthesized using bottom-up and top-down techniques. Reproduced with permission from Ref. [78] Copyright 2024, Elsevier. (g) Different arrangement of single atoms on a support leads to distinct degrees of atomic exposure. Reproduced with permission [79] Copyright 2020, American Chemical Society. (h) Schematic showing typical M/N/C catalysts: single-atomically dispersed TM-N-C, metal nanoparticles wrapped in N-doped carbon (TM@NC), and a combined structure with both TM-N-C and TM@NC. Various defects in carbon materials: (i) Vacancies, holes, edge defects, and nitrogen Edge defects, and (j) (M-N-C) and (M – C), and nitrogen site vacancies.

current density for a certain by-product. A Tafel slope of 118 mV dec⁻¹ indicates that the initial electron transfer is the ^{*}CO₂⁻ formation and it is regarded as RDS for electroreduction of CO₂. On the other hand, for values of the Tafel slope near to 59 mV dec⁻¹ is interpreted as being controlled by the following electron transfer step that leads to ^{*}*COOH formation [77]. Even though C₂⁺ products usually have higher market price and are industrially more specialized than those from C₁, the selectivity of CO₂RR over these determinants is still much lower. C₂⁺ product formation is intrinsically difficult due to the requirement of C-C coupling or dimerization, which in turn requires an active site in proximity to the reaction intermediate. However, the majority of SACs show isolated separated active sites which may hinder C-C bond formation and lead to only small amount of multicarbon products. However, for the majority of dual-atom catalysts, it is their architecture that gives rise to adjacent active sites for efficient C-C coupling for the exogenous production of C₂H₄, a most desired fundamental chemical feedstock for polymer and petrochemical industries (and its generation in CO₂RR can take two different mechanistic pathways). The first one is via coupling of two adjacent CH₂ exposed on surface to give C-C dimerization. The second route involves CPET from an ethylene oxide intermediate (^{*}OCHCH₂) which is then reduced to give ethylene. Such reaction pathways need to be in competition with the production of C₂H₅OH, a second major product of CO₂RR [77]. Alternatively, ethanol can be generated by direct protonation of oxygen sites in an ^{*}OCH₂CH₂ intermediate which then progresses to further reduced state to form the alcohol. The competition between these two pathways highlight the

intrinsic challenge for high selectivity of targeted C₂⁺ products on SACs. These limitations can be addressed by developing advanced catalyst design strategies that are effective in adjusting the electronic environment of active sites, generating multi-atom coordination structures, or engineering cooperative backyard environments for stabilizing the key intermediates and selectively accelerating C-C coupling.

4. Atomic structural engineering of SAC-based cathodes for enhanced CO₂ reduction

The primary mechanism of Zn-CO₂ batteries is the CO₂RR, driven by a set of chemical reactions of the zinc anode and CO₂. The three-phase reaction mechanism, CO₂-electrolyte-cathode, is linked to the extremely complicated CO₂ electrochemical process on the cathode compartment of Zn-CO₂ batteries. Therefore, to achieve rational battery designs, particularly in the cathode compartment, it is imperative to clarify the basic process of CO₂ electrochemistry. Various advantages of SACs are already elucidated in the previous sections however, it is important to address the challenges that limit the true potential of SAC-based cathodes in Zn-CO₂ battery, which include (i) stability, (ii) intrinsic active sites, (iii) scalability, and (iv) defect engineering and coordination of SACs [81,82]. In general, the performance of catalysts was analyzed using parameters such as a Faradaic efficiency,

$$FE (\%) = \frac{nF.N}{Q} \times 100$$

where n denotes the number of electrons exchanged for product formation, N represents the number of moles for a selective product (mol), F (Faraday constant) = 96,485 (C mol⁻¹) and Q is the total charge passed (Coulombs). To estimate overpotential (η) from voltametric studies tafel slope analysis ($\eta = a + b \log i$) is carried out. Another important parameter for CO₂ derivative product formation is the turnover frequency (TOF) which is given as,

$$\text{TOF} = \frac{(J \times A) / (N_e \times F)}{M_c \times (\omega / m)}$$

where J represents partial current density for product production, A denotes area of the working electrode, N_e is electron transfer number, F (Faraday constant) = 96,485 (C mol⁻¹), M_c denotes mass of catalyst loaded, ω (%) is content of metal in the SAC, and m denotes atomic mass of metal in SAC.

4.1. Stability of SACs under electrochemical conditions

The stability of an electrocatalyst is affected by various factors, including its composition, morphology, electrical conductivity, structural characteristics, surface area, and particle size. Among these, particle size plays a particularly vital role in finding the durability of the electrocatalyst. The shape and proportion of the particles influence the driving force for metal nucleation and growth during the initial stages of catalyst formation. The decrease of particle size endows particles with higher specific surface area, thus reducing the reaction barrier and improving their catalytic performance [83,84]. For SACs, the larger surface area with higher surface free energy promotes isolated atoms clustering. However, as the support surface is filled up with metal atoms, these cannot just stay isolated anymore and rather agglomerate into nanoclusters since they present a high-energy surface. This tendency toward aggregation is the main hindrance for obtaining high metal loading in SACs. As a result, the metal loading in most SACs is low (usually less than 3 wt%) to avoid aggregation. Proper choice of precursors and controlled synthesis are both critical in fabricating high-efficient SACs so as to maximize the metal loading while keeping excellent atomic dispersion, special surface area on metallic carrier substrate [85].

4.1.1. Controllable synthesis and uniform distribution of single atoms

In order to fabricate isolated single atoms of high stability, accurate synthetic methods are required. In the formation process, carrier precursors can confine, diminish and fix metal atoms. Theoretical researchers have found two important factors which are helpful to promote the loading of metal atoms and inhibit agglomeration. These comprise increasing the exterior area of the carrier and promotion of stronger interaction between the metal atoms and the carrier surface [78,83]. These principles have guided the development of various SAC synthesis methods, such as bottom-up approaches and top-down approaches. Fig. 3(e) represents four synthesis methods under bottom-up approaches, such as co-precipitation, atom layer deposition (ALD), impregnation, and deposition-precipitation. In the co-precipitation method, simultaneous precipitation of metal and support precursors restricts the metal atoms within the support matrix and lowers atomic utilization. The metal precursor in the impregnation method is anchored on the support material through an adsorption technique. Impregnation leads to metal aggregation during thermal treatment. ALD method precisely deposits material in one atomic layer at a time, as it follows the self-limiting gas-phase reaction (self-saturating surface reaction). It provides atomic control with uniform active site density for stable SACs. Deposition precipitation allows metal precursor deposition via a slow pH change. Top-down approaches (Fig. 3(f)) include pyrolysis, *anti*-Ostwald ripening, mass-selected soft-landing technique, and high-temperature atom trapping approach [78]. From the top-down approach, pyrolysis involves thermal decomposition of metal-organic

precursors under an inert atmosphere, and *anti*-Ostwald ripening, with its stabilizing mechanism, improves metal-support interaction. In mass-selected soft-landing, the metal is deposited onto a support under high vacuum conditions. In the high-temperature atom trapping method, the large particles are atomized via thermal treatment and trap a single atom on the defect site of the support material. In comparison, the ALD method assures atomic precision and high uniform distribution of single atoms in the bottom-up approach, and in the top-down approach, pyrolysis was highly practiced for its simplicity and scalability for high-loading of SACs.

Further, it is also important to understand the ways in which a single atom can be positioned on the catalytic support material. Fig. 3(g) shows varying configurations of a single atom in a catalytic reaction. Type 1: Single metal atom is dispersed on the surface (interaction between surface anchor sites) of the supportive material [79]. This type of surface dispersion has moderate stability due to the higher chance of aggregation, and in type 2, the metal atom substitutes the exterior atoms of the substrate. The substitution of the single metal atom chemically incorporated in the substrate by replacing the carbon atom to form a stable coordination site creates a slightly higher impact on stability. In type 3, the metal atom forms a coordination with bridging ligands, and it tunes the electronic structure in ligand design. In type 4, the single-atom anchors on the metal-organic framework (MOF) control the dispersion of atoms with a high active site density. It avoids aggregation and mitigation of single atoms due to its confined framework [86]. The single atom gets trapped during the surface substitution and the organic framework becomes highly stable with a unique electronic structure, and this leads to an increase in the activity of active sites. In addition to various synthesizing methods and positioning of SACs, the design of supportive material for metal atom are equally crucial. The stability of central metal and CO₂ reduction performance were determined by the surroundings of the isolated metal atom.

4.1.2. Metal-support interactions (MSI) and confinement for long-term stability

The concept of metal-support interactions (MSI) was first introduced by Tauster et al. who demonstrated that the chemical linkage of noble metals and TiO₂ significantly enhances catalytic activity [87]. Following this discovery, extensive research has been directed to the study and manipulation of these interactions to create very efficient heterogeneous catalysts. According to the support types, SACs can be divided into two major groups namely C-supported and non-C-supported SACs. Among C-based SACs, the trapped metal atoms are anchored on carbon matrices and nitrogen-doped carbon matrices such as carbon quantum dots, graphene frameworks, graphene oxide, g-C₃N₄, graphdiyne, and carbon nanotubes. In such systems, nitrogen is a Lewis base, and the metal behaves as a Lewis acid, which constructs coordination connections between N and M to favorably disperse single-metal atoms firmly embedded in the carbon skeleton [88]. Here, ultimately nitrogen acts as an eminent heteroatom for the C-supported SACs in CO₂RR. The coordination of transition metals is a well-established strategy for modulating the surface catalytic properties of SACs. The study of coordinated structures has become an essential aspect of catalyst design and characterization, which contributes to stabilizing single metal atoms and preventing their aggregation. Considering the catalytic site framework, transition-metal nitrogen-doped carbon (TM-N-C) can be divided into three categories (Fig. 3(h)). The first category consists of C-supported metal nanoparticles enclosed in nitrogen-doped carbon shells (denoted as TM@NC), where metal and nitrogen co-activate carbon sites are typically identified as the active center. The second category involves a combination of both nanoparticles and an anchor of single atom to the nitrogen sites (TM-N-C@TM@NC). In the third group, SACs are represented as individual transition metal centers anchored via nitrogen coordination through a carbon matrix, i.e., TM-N-C. In this aspect, the TM-N_x moieties are generally considered as the CO₂RR active sites [89].

4.1.3. Defect engineering

In addition to direct influence on the electrochemical processes, they also operate as unique anchor sites to trap metal species and enhance both the selectivity and stability of SACs for better catalytic performance. The imperfections of defective sites on metal-based or carbon-based materials can be used to load isolated atoms and thus prevent them from moving together. These defects can be broadly categorized into i) Intrinsic Defects: The ones that are formed naturally under normal conditions of carbon framework such as vacancies, edges, lattice distortions and topological defects. ii) Extrinsic Defects- These involve dopants, such as nitrogen heteroatom and atomically dispersed metal sites, which tune the local electronic configuration and boost catalytic properties [87].

Defective carbon structures are characterized by a wide range of imperfections, including single and double vacancies to porous voids. Further edge defects and heteroatom doping, specifically nitrogen coordination, help in the enhancement of active sites in catalytic behavior as depicted in Fig. 3(i). As illustrated in Fig. 3(j), the interaction of M-N-C and Metal-Carbon (M – C) frameworks is critical. The nitrogen doping creates multiple active site environments, such as graphitic N (bulk and edge), pyrrolic N atom, pyridinic N atom, and pyridinic N oxides [90]. These defects serve as anchor points for a single atom, as well as

maintain electronic structure and adsorption of intermediates in the reactions. Consequently, modulation of defect types, dimensions, and spatial distribution of active sites can greatly influence the CO₂ activation and rate of the reaction.

4.2. Modulating intrinsic active sites for selective CO₂ reduction

To address the inherent limitations of low active sites in SACs, a critical strategy involves enhanced intrinsic activity of each isolated site to maximize overall electrochemical performance. Although various strategies have been attempted to design active sites, regulate coordination environments, and enhance structural support toward electrocatalytic reactions, the intrinsic mass activities of SACs are still not sufficient to be compared with commercial catalysts [91]. The electronic effect and coordination geometry around the central metal played a crucial function in the catalytic efficiency of SACs. Hence, it is necessary to design the coordination geometry and regulate the state of active sites for enhancing their electrocatalytic performance only be achieved by proper adjustment of the catalysts. Atomic-scale metal species in SACs, modified and stabilized on semiconductor supports, also have well-defined coordination but are coordinatively unsaturated with the semiconductor substrates as the main active center. The local

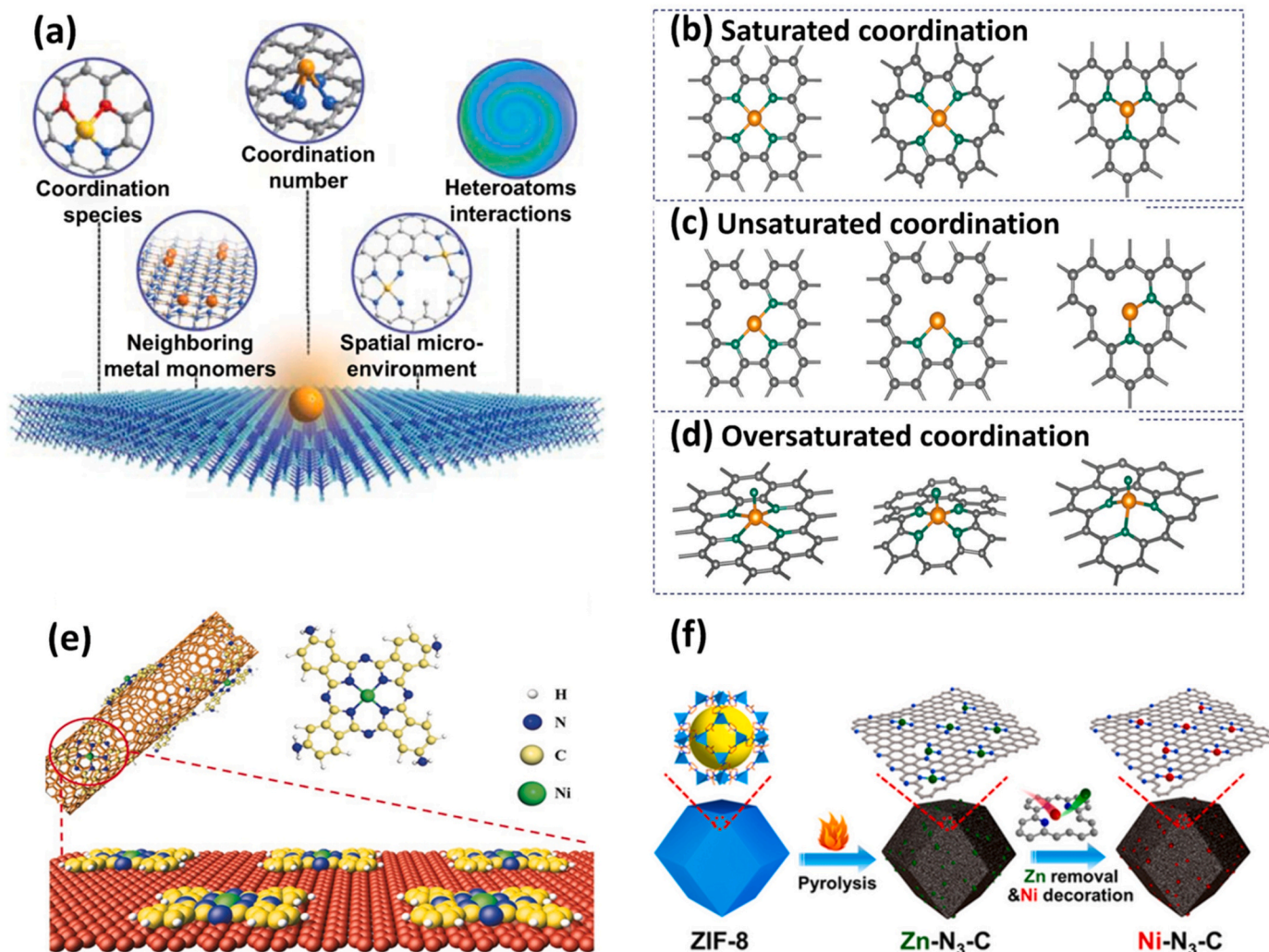


Fig. 4. (a) Techniques to design the coordination sphere of isolated single-atom sites. Reproduced with permission from Ref. [93] Copyright 2021, Springer Nature. Summary of reported coordination structures with (b) saturated coordination, (c) unsaturated coordination, and (d) oversaturated coordination. Reproduced with permission from Ref. [91] Copyright 2024, John Wiley and Sons. (e) Synthesis of model Ni SACs for the CO₂RR. Reproduced with permission from Ref. [94] Copyright 2020, John Wiley and Sons. (f) Synthesis of single-atom Ni electrocatalysts by the (PSMS) strategy. Reproduced with permission from Ref. [95] Copyright 2021, John Wiley and Sons.

coordination is very important in influencing geometrical and electronic properties of SACs, since the activity of isolated metal atoms is related to the ionic and covalent interactions with a substrate [92]. Development of efficient SACs remain a challenging subject due to the compromise among high stability, uniform active sites and tunable electronic/geometry properties. The bottleneck is represented by the stabilization of such independently very reactive metal centers as highly dispersed ones, due to an extremely high surface energy. Therefore, to address these challenges, research is focused on strategies for stabilization and confinement of individual metal atoms. The adjacent atoms in SACs, through intense electronic coupling, it modifies the catalytic active center. Hence, with precise modulation of the coordination sphere around the catalytic center, we can impact the intrinsic activity and durability of SACs, accelerating their development to meet the demands of various reactions [93]. Fig. 4(a) suggests a number of methods, including coordination species, coordination number, heteroatoms interaction and neighbouring metal monomers together with spatial micro-environment to address the problems associated with poor active sites in SACs and thus maximising their catalytic activity [93].

The coordination atmosphere of SACs can be efficiently modulated by adjusting the atomic radius and electronegativity of hetero-atoms doped into carbon network. The coordination structure can be accurately controlled by modifying the types of heteroatom and doping methods, which has an enormous effect on the catalytic performances of SACs [96]. Moreover, heteroatoms cannot solely promote the inherent properties of a host material but also offer an economy-effective approach to stabilize metal atoms. Mechanically strong metal-support interactions are necessary because there is a lack of lone-pair electrons in sp^2 carbon that causes weak binding, resulting in high diffusional mobility and tendency to agglomerate of the metal atoms.

4.2.1. Electronic regulation of SAC via nitrogen coordination

Nitrogen is often doped as a coordination element, during which the nitrogen atom with high electron negativity could enhance metal-atom binding and induce a positive shift of electronic structure to enhance the electrocatalysis. It provides the electron cloud flow from metal atoms to nitrogen atoms, leading to a partially positive charge on the central metal atom, and even partial positive charge of neighbouring carbon atom. In addition to nitrogen, heteroatom functionalization forms N-substitution complexes through, oxygen, sulfur and boron as well as phosphorus and chlorine to form disparate derivative structures compared to other $M-N_4$. These modifications modify the oxidation state of the core metal atom and change the charge densities over active sites, exerting great influence on catalytic activity [97]. M-N-C frameworks were classified into saturated, unsaturated, and oversaturated coordination as shown in Fig. 4(b–d). In this arrangement, metal sites spread as a film on the surface of the substrate and their electronic structure becomes fully occupied in a saturated state as shown in Fig. 4(b). Obviously, the unsaturated coordination involves breaking the balanced structure pattern by removing one or two coordinated nitrogen atoms, which would bring the metal sites above the carbon plane and accordingly enhance their exposure to reactant molecules in being adsorbed. Additionally, asymmetrical coordination structures can lead to the strengthened local electronegativity at a single metal site as seen in Fig. 4(c). Another successful approach is the establishment of oversaturated coordination geometries (e.g., $M-N_5$) which deviate from this saturated electronic equilibrium within $M-N_4$. As depicted in Fig. 4(d) oversaturated complexes often possess higher valent metal sites than their unsaturated analogues [91]. This increased electronegativity promotes the efficiency of electrolysis reactions as a higher valence for central metal atoms, the better performance of catalysts.

One common approach to realizing such confinement is by use of core-shell type structures with sharp structural interfaces between the core and the shell. Liu et al. synthesized Ni single atomic catalysts by high temperature reaction with two steps. Fig. 4(e) shows the structure

of Ni-TAPC (Nickel (II) 2,9,16,23 tetra (amino) phthalocyanine) with a composition of NiN_4 moiety. Here, Ni-TAPC is covalently attached to CNT by means of the C-C coupling. The C-C coupling bonding was introduced to improve the charge transfer and catalytic stability [94]. By tuning the coordination geometry, Wang et al. studied different N moiety with Co catalysts Co- N_4 and Co- N_2 [98]. The heteroatoms of MOF ligands are profoundly involved in immobilizing the metal atoms and keep them from flowing during high-temperature pyrolysis. Such structural robustness permits the creation of MOF-induced SACs that possess not only excellent performance inherited by parent MOFs in catalysis but also are free from shortcomings of pristine MOF (e.g., low conductivity, weak catalytic activity). For the past several years, the MOF-derived SACs have emerging with increasing interest in energy-related electrocatalysis and this is ascribed to their capabilities of supplying well-defined, abundant pore structure, high surface area, modifiable organic ligand, and strong metal-support interaction. Embedding a single atom through nitrogen heteroatom linkage upgrades the metal nodes and makes them very attractive for fuel cells, water splitting, and CO_2 reduction reactions [99]. A facile post-synthetic metal substitution (PSMS) strategy was implemented by Zhang et al. to create a less-coordinated single-atom Ni catalyst (Ni- N_3 -C) for high performance. The process involved pyrolyzing Zn-MOF to obtain a N-doped carbon substrate with Zn vacancies (Zn- N_3 -C), followed by removing Zn and replacing it with Ni, as illustrated in Fig. 4(f). The 0.58 wt% of metal loading decreases the $^*COOH$ activation energy compared to Ni- N_4 -C. The resulting Ni- N_3 -C catalyst provides FE_{CO} (95.6%) and TOF ($1425\ h^{-1}$) for CO_2 reduction, outperforming other Ni-N-C catalysts. Its CO selectivity (over 90%) and stability in a Zn- CO_2 battery demonstrate its potential for practical energy conversion systems [95].

4.2.2. Spatial confinement of MOF/ZIF-derived framework for SAC stabilization

The spatial confinement acts as the best strategic role in preparing single atom to anchor on nitrogen doped carbon matrix. Hence, to increase the active metal site, excess nitrogen sites are needed, and this was satisfied with the zeolite imidazolium salt framework (ZIF). Here, the center metal coordinated with the imidazolate ligand, which is used as basic MOF precursor due to its abundant N sites. A widely adopted chemical strategy for SAC synthesis involves the carbonization (one-step pyrolysis) of ZIF containing transition metals, such as Co in ZIF-67 and Zn in ZIF-8. While these approaches have demonstrated feasibility, as shown in Fig. 5(a), their practical applications are limited by low yields and metal anchoring ($\sim 1\ wt\%$). Achieving SACs with high metal loadings are essential for real-world applications. Furthermore, current chemical methods lack flexibility and are challenging to modify for synthesizing SACs with different transition metals. A promising alternative is the ligand-mediated synthesis approach, which has successfully produced metal-SACs with metals including Pt, Ru, Fe, Zn, Ni, Co, Mn, and Cu [100]. Nevertheless, as the sub-nanometre particles were more mobile and diffusive when integrating into SACs, greater progress is required to ensure their universality in the synthesis of SACs and precise microstructural manipulation. Changming et al. prepared the ZIF-assisted pyrolysis approach for the synthesise of Ni single atoms anchored in nitrogen doped porous carbon, showing high performance toward CO_2 reduction. The material was pyrolyzed in an argon environment at $1000\ ^\circ C$, resulting the growth of a nitrogen-doped carbon framework derived from organic linkers. N-doped carbon could reduce weight at $900\ ^\circ C$ because of the escape of Zn species all with a low boiling point for $907\ ^\circ C$. Fig. 5(b) shows the Zn evaporation generated vacancies, which were easily filled with Ni^{2+} ions and obstructed aggregation. The coordination of Ni^{2+} with nitrogen further stabilized the isolated metal atoms, while the surrounding carbon structure enhanced their stability. Electrochemical evaluation showed that the overpotential of Ni-SACs is $0.89\ V$, and FE_{CO} exceeded 71.9% , significantly outperforming Ni nanoparticles (Ni-NPs), as shown in Fig. 5(c). Additionally, the TOF of single Ni sites reached $5273\ h^{-1}$ as shown in Fig. 5(d).

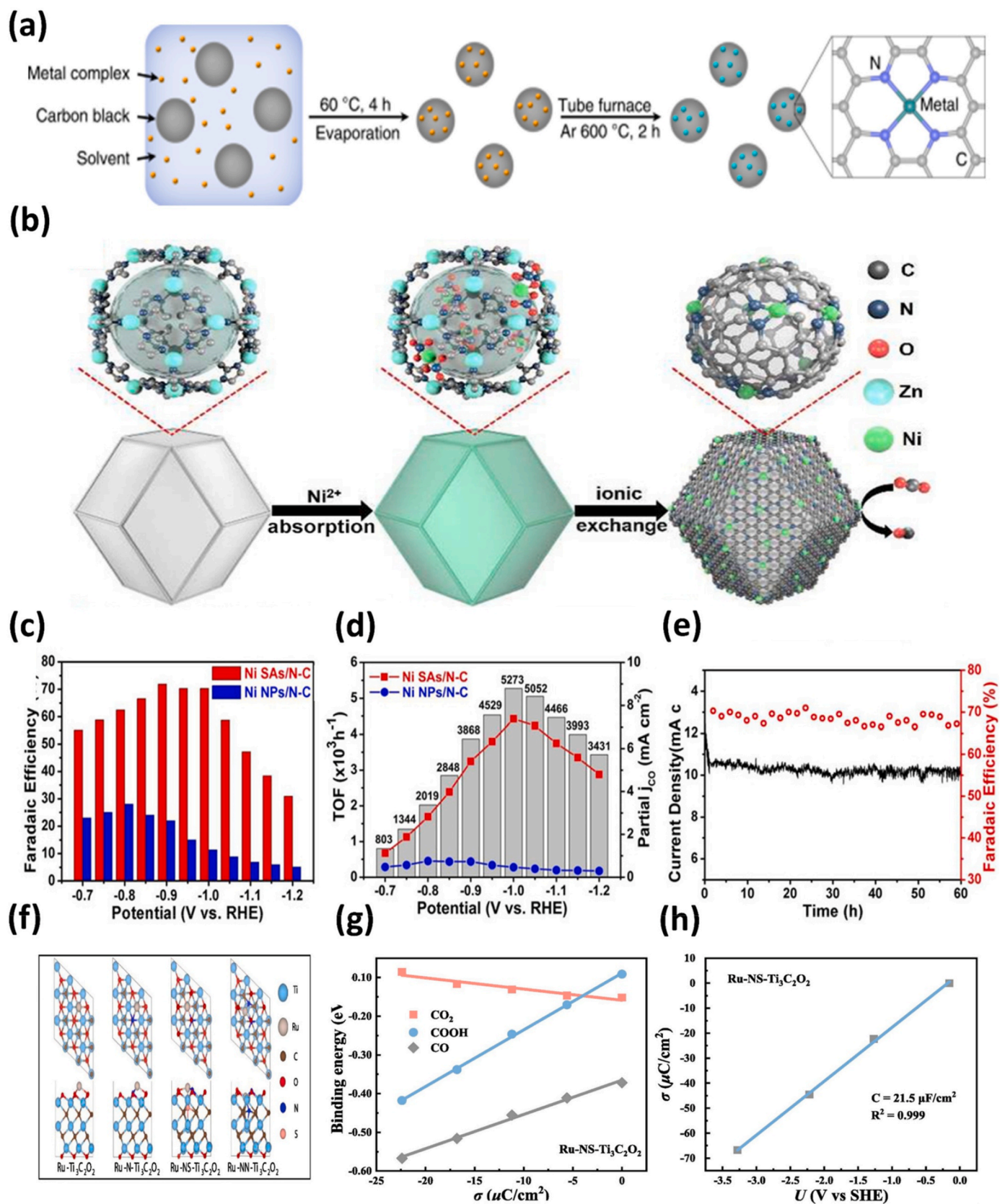


Fig. 5. (a) A universal two-step synthesis procedure in the preparation of metal-SACs. Reproduced with permission from Ref. [100] Copyright 2019, Nature. (b) Formation of Ni SAs/N-C, (c) FE of CO, (d) partial CO current density plots and TOF of Ni SAs/N-C and Ni NPs/N-C at various applied potentials, and (e) Stability of Ni SAs/N-C for 6 h at a potential of -1.0 V vs RHE for Ni SAs/N-C. Reproduced with permission from Ref. [101] Copyright 2017, American Chemical Society. (f) Optimized structures of Ru-Ti₃C₂O₂, Ru-N-Ti₃C₂O₂, Ru-NS-Ti₃C₂O₂, and Ru-NN-Ti₃C₂O₂, (g) Binding energy of CO_2 , COOH, and CO, (h) Plot of surface charge density (σ) as a function of computed electrode potential (U) - Helmholtz capacitance (C_H). Reproduced with permission from Ref. [103] Copyright 2023, Elsevier.

Long-term stability tests, as depicted in Fig. 5(e), demonstrated no decay in FE over 60 h of continuous operation [101]. Similarly, to develop an atomically dispersed Co electrocatalyst for CO₂-to-CO conversion, Pan et al. introduced an N-coordination strategy. They synthesized hollow N-doped porous carbon spheres (HNPCs) from polymers, which have a large surface area of 568 m² g⁻¹ and rich nitrogen binding sites. Atomically dispersed Co sites were anchored onto these structures, followed by pyrolysis at 700 °C under an Ar environment to produce SiO₂@N-doped porous carbon morphologies [102]. It is observed that the SACs, synthesized via the pyrolysis method, are cost-effective and provide high homogeneity in the distribution of single atoms. The thermal treatment enhances the formation of anchoring sites (nitrogen-coordination) and traps the metal on the support matrix.

4.3. Alternative support matrices

The most stable form of metal-support interaction in SACs is covalent metal-support interaction (CMSI), which involves the strong covalent bonds that are formed between the support and metal atoms. This tendency is especially observed in the non-C-supported SACs, including mxene, metal oxides (or hydroxides), and metal-derived compounds. These materials have a high concentration of Lewis base-like coordinated atoms, which provide strong covalent bonding with isolated metal atoms. In non-C-supported SACs, the strong metal-support interactions stabilize the catalysts, facilitate higher loading of metal atoms and result in superior catalytic efficiency [104,105]. Cao et al. studied the performance of Ru atoms and various MXene supports, for example, Ti₃C₂O₂, single N-doped Ti₃C₂O₂, N, S co-doped Ti₃C₂O₂, and N, N co-doped Ti₃C₂O₂. Fig. 5(f) shows the coordination architecture of Ru SACs. Ru atom is fixed to the vacant location of O atoms in Ru-Ti₃C₂O₂ with Ru-O bonds at 2.067 Å. In the Ru-N-Ti₃C₂O₂ system, one oxygen atom is replaced by a nitrogen atom, with the Ru atom remaining at the vacant area. The bond lengths of Ru-N and Ru-O are measured at 1.889 Å, 2.039 Å, and 2.048 Å, respectively. This coordination environment shows effective tuning of the electronic and geometric structure of the Ru single atom. The correlation between binding energy (*E_b*) and surface charge density (*σ*) is seen in Fig. 5(g). The association between the binding energies, *E_b* (CO₂), *E_b* (COOH), and *E_b* (CO) and *σ* is linear. For CO₂, COOH, and CO, the dipole moment (*μ*) of the adsorbates is -0.003, 0.015, and 0.009 eÅ, respectively, as indicated by the slopes of these lines. Equation (1) determines the relationship between electrode potential *φ* and surface charge density *σ* as given below:

$$\phi = 1/C_H \sigma + \phi_{PZC}$$

where *C_H* represents differential Helmholtz capacitance and *φ_{PZC}* represents zero charge potential. The data point *σ*-*U* can be accurately characterized by a linear fit, as shown in Fig. 5(h), suggesting that *C_H* might maintain a constant. *C_H* and *φ_{PZC}* are found to be 21.5 μF/cm² and -0.15 V versus SHE [103]. While observing the catalytic performance of SACs with their electronic and geometric structure of metal and support, such as C-supported matrix and non-C-supported matrix, a carbon-supported matrix derived from MOFs offers a superior advantage of stable anchoring of the metal atom active site. It also achieves high conductivity and a large surface area for effective CO₂ adsorption and mass transport.

4.4. Modification of SAC by functionalized heteroatoms (N, O, S, and P)

Functionalization with nitrogen has also been heavily researched as they can be readily synthesized and are stable under high potential conditions. These materials possess various defect kinds (including cation and anion vacancies) that promote metal-support interactions and as a result, the dispersion of SAC. reactivity and energy-derived structure. The dynamic evolution of defect structures during the catalytic reactions is very important for tailoring performance [106]. For

example, single-atom Cu sites were hosted in graphdiyne (GDY), and had been able to efficiently coordinate through the Cu-C bonds via preventing atom agglomeration while offering efficient electron transfer pathways during CO₂-to-CH₄ conversion. The data of X-ray absorption near the edge structure (XANES) and Extended X-ray absorption fine structure (EXAFS) show that Cu-single atoms (SAs) are cationically oxidized and form C-Cu bonds in Cu-SA s/GDY [107]. Similarly, Dong et al. showed that selective etching of pyridinic-N and pyrrolic-N from 3D N-functionalized porous carbon introduced topological defects, thereby promoting the performance of SAC [108]. In another study, cobalt single atoms were immobilized on defective nitrogen-doped carbon macro-porous fibers (Co-SAs@NCMF). When subjected to high-temperature treatment, Co²⁺ ions are thermally reduced to Co nanoparticles which are then agglomerated into atomically dispersed Co sites at 1000 °C. These Co atoms are stabilized within C and N vacancy sites, resulting in a high density of active sites, as illustrated in Fig. 6(a). Elemental mapping further confirms the even dispersion of C and N, while Co atoms exhibit localized clustering as depicted in Fig.

6(b). Co-SAs@NCMF catalyst exhibits an outstanding FE_{CO} of 98.4% and a high TOF of 38,390 h⁻¹ at -1.0 V vs. RHE, demonstrating superior CO₂ reduction activity. The AC HAADF-STEM images of Co SAs@NCMF reveal the uneven distribution of Co sites, which vary across different fiber regions as shown in Fig. 6(c) [109]. The nitrogen functionalized surrounding provides an unsaturated coordination for single atom, especially in pyridinic-N, in which the lone pair of electrons lowers the CO₂ adsorption energy and enhances the CO₂RR performance in Zn-CO₂ battery. The adsorption and desorption of the intermediates directly depend on the coordination environments of the central metal with the surrounding ligands in the first shell in CO₂ reduction [111].

The ligand effect varies with the different heteroatoms other than nitrogen. The replacement of oxygen as a heteroatom provides a tremendous decrease in the energy barrier for *COOH intermediate and an increase in the *CO adsorption, in Fe-SACs with FeN₂O₂ coordination geometry. Compared to FeN₄ sites, due to the higher electronegativity of oxygen atom, FeN₂O₂ provides 95% of CO selectivity with the potential range of -0.4 to -0.8 V [112]. Han et al. and their groups worked on the sulfur-incorporated atoms onto a carbon substrate and fabricated FeSNC catalyst, which facilitates (CO₂RR) activity and stability, ascribed to its geometric environment and enhanced adsorption of reaction intermediates. The polymerization of Fe-tetrahydroporphyrin (Fe-TThP) was catalyzed by FeCl₃. Finally, FeSNC material was obtained with hierarchical pores by heating it to high temperatures (pyrolysis) and then etching it, as shown in Fig. 6(d). The prepared FeSNC has a typical rod-like structure of the original Santa Barbara Amorphous-15 (SBA-15) (Fig. 6(e)) in SEM images, and TEM images (Fig. 6(f)) confirmed that FeSNC has a well-ordered micro-mesoporous structure. An isolated bright spot of (Fe single atom) scattered throughout the carbon material is seen in the AC-HAADF-STEM technique (Fig. 6(g)). The XANES spectrum of FeSNC and several reference materials like iron foil, commercial iron phthalocyanine (FePc), Fe₂O₃, and FeS₂ are shown in Fig. 6(h). It achieves a remarkable CO selectivity of 94.0% at -0.58 V versus the RHE and reaches a peak partial current density of 13.64 mA cm⁻² at -0.88 V [110]. Additionally, when utilized as a cathode material in a Zn-CO₂ battery, FeSNC delivers a high-power density of 1.19 mW cm⁻² with steady charge-discharge cycling performance. For the first time, the polyhedron-shaped Fe-P@NCPs bifunctional electrocatalyst for rechargeable aqueous Zn-CO₂ batteries was documented. Utilizing in-situ-templated ZIFs with a calcination process, the Fe-P sites bonded with N-doped carbon polyhedrons were generated simply and efficiently. The resulting catalyst demonstrated good OER performance for O₂ generation in addition to high aqueous CO₂RR activity with FE_{CO} of 95% at -0.55 V and an overpotential of 430 mV. The constructed Zn-CO₂ batteries with the Fe-P@NCPs cathode demonstrated minimal deterioration with respect to discharge voltage over 7 days, with cycling durability over 500 cycles and a peak power density of 0.85 mW cm⁻².

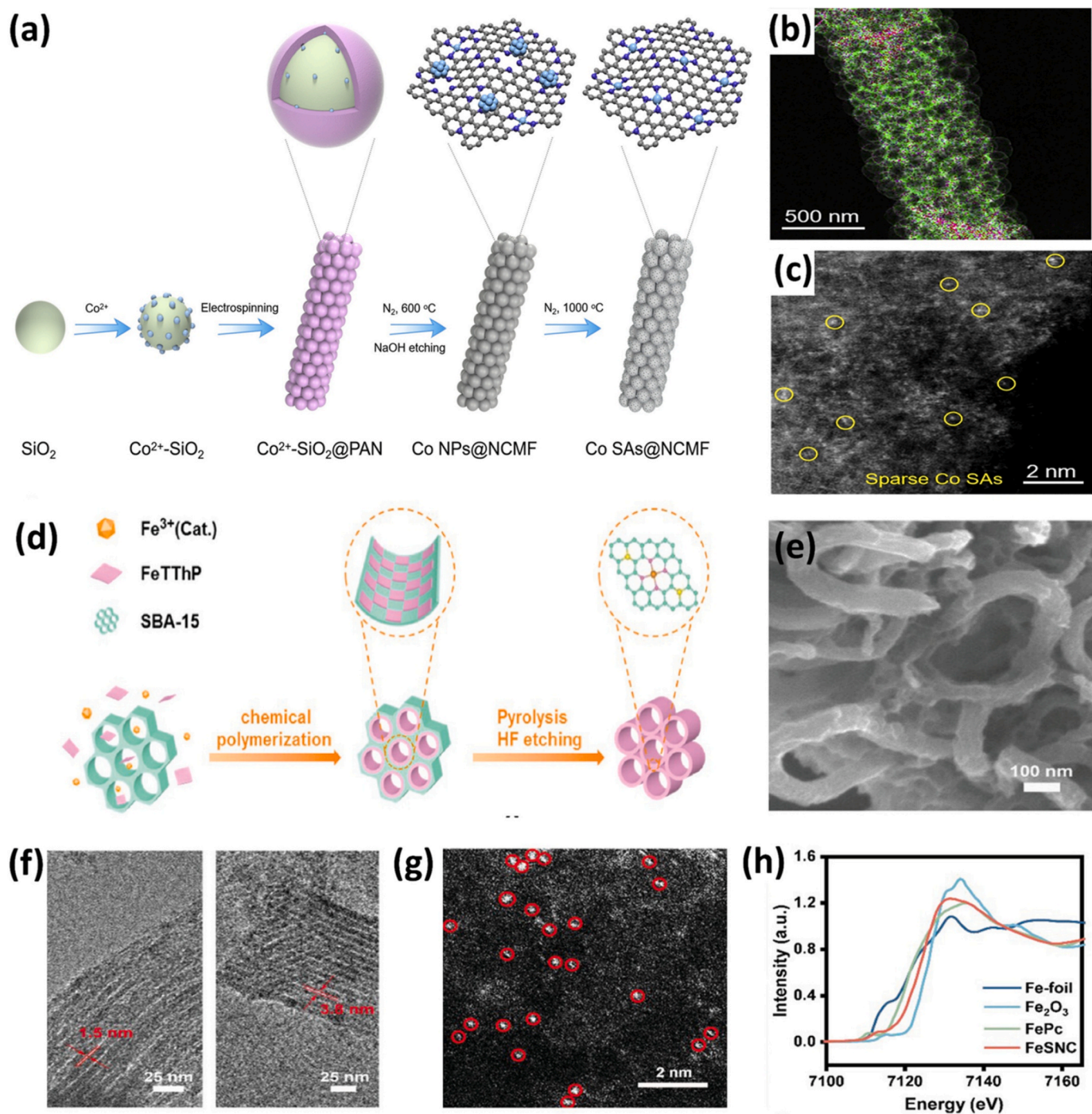


Fig. 6. (a) Synthesis of Co SAs@NCMF, (b) Overlay image Co SAs@NCMF, and (c) AC-HAADF-STEM images of Co single atoms in the dense area and sparse area. Reproduced with permission from Ref. [109] Copyright 2022, Elsevier. (d) Synthesis of FeSNC, (e) SEM image, (f) TEM images, (g) AC-HAADF-STEM image of FeSNC, and (h) WT k^2 -weighted EXAFS contour plot of the FeSNC. Reproduced with permission from Ref. [110] Copyright 2024, John Wiley and Sons.

The presence of highly catalytic Fe-P nanocrystals helped to achieve power density of 0.85 mW cm^{-2} in the battery and is responsible for its great selectivity and efficiency [113]. Both S and P functionalization, along with the N, finely tune the electronic surrounding of single atom, creating structural strain for regulating the binding energy of intermediates.

4.4.1. Axial coordination of heteroatoms in SACs for selective CO_2 reduction

The heteroatom ligands at the axial position enhance the mechanistic

landscape of the CO_2 reduction through precise electronic and orbital reconfiguration of the active metal center. An electron-donating axial ligand increases the electron richness on the central metal, enabling it more nucleophilic. This enhanced electron richness facilitates the initial CO_2 activation, where the linear CO_2 molecule bends upon adsorption ($\text{CO}_2 \rightarrow \text{OCO}^-$), as the metal's filled d-orbital follows the "push" electron density into CO_2 antibonding π^* orbitals, weakening the C=O bonds and lowering the overpotential. The axial coordination can decouple the binding affinities of key intermediates by adjusting the metal-carbon bond strength; the Gibbs free energy of the transition state for $^*\text{COOH}$

formation is minimized. Further axial ligands introduce a localized geometric environment that specifically stabilizes the polar $^*\text{COOH}$ via electrostatic interactions without over-binding the $^*\text{CO}$, which ensures easy release of the by-products. This selective stabilization of $^*\text{COOH}$ maintains weaker CO binding, which fits the Sabatier principle and can be explained by the changes in the d-band caused by axial coordination at the single-atom site [114,115]. Introduction of axial coordination to the single atom can be theoretically understood based on the Sabatier principle, d-band center theory, and orbital orientation. Generally, the d-band theory and Sabatier principle explain the changes in adsorption strength and the importance of moderate binding for better activity. According to the Sabatier principle, the key intermediate adsorption should not be too strong or too weak for effective catalyst engineering. In planar coordination, strong adsorption results from a higher d-band center, which enables hydrogen adsorption and leads to HER. In axial coordination, the weak adsorption makes hydrogen binding thermodynamically less favourable, thereby suppressing HER. Based on the d-band theory, the binding affinity of intermediates depends on the transition metal d-band center's position, which is relative to the Fermi level. Here, axial coordination plays a critical function in withdrawing the electron density from the transition metal, leading to a downshift of the d-band center, which weakens the overlap of 3d orbitals and orbitals of adsorbed species. Orbital hybridization causes a synergistic bonding effect (back-donation), which brings changes in CO binding behavior [116]. Although the inner-plane coordination stabilizes the metal atom by anchoring to its co-planar configuration, it still has the challenge of atomic diffusion, which leads to aggregation under reaction conditions.

Axial coordination suppresses atomic diffusion by significantly raising the migration energy barrier (E_{diff}) through enhanced metal-support anchoring, stronger orbital hybridization, electron withdrawal that elevates the metal valence state, and a vertical pinning effect that rigidly fixes the atom against surface hopping. DFT calculations show this increases E_{diff} from ~ 1 to 2 eV in planar MN_4 to >2.5 eV in axial configurations, preventing aggregation even under electrochemical bias or at higher loadings. Further, there is a need for advancement of the outer-plane coordination geometry of SAC to avoid atomic diffusion and to improve the slow kinetics of CO_2 reduction. Hence, axial coordination is introduced into the symmetric planar structure of SACs [117]. In particular, the axially positioned heteroatom modifies the electronic arrangement in the planar configuration and disturbs the active site symmetry. The axially linked atom converts the confined geometry to 3D coordination by modifying the spin configuration, metal valence state, and d-band center. Eventually, it resolves two major issues faced by the SACs in CO_2 reduction. The axial coordination follows a mechanism of donation or withdrawal of electrons from the metal center, and it leads to a shift in the metal d-orbital. This strengthens the coordination of the metal and support, forming a vertical stabilization pathway that suppresses the atom diffusion and aggregation. In the electrocatalytic process, dynamic metal-support bonding to lock in atomic diffusion suppression refers to the bond length, coordination number, or local strain at the metal-support anchor site that can adjust under operating potentials. The overall coordination environment of the single-atom catalyst remains intact to kinetically suppress atomic diffusion, and reversible modulation has been observed in the in-situ XAS (XANES and

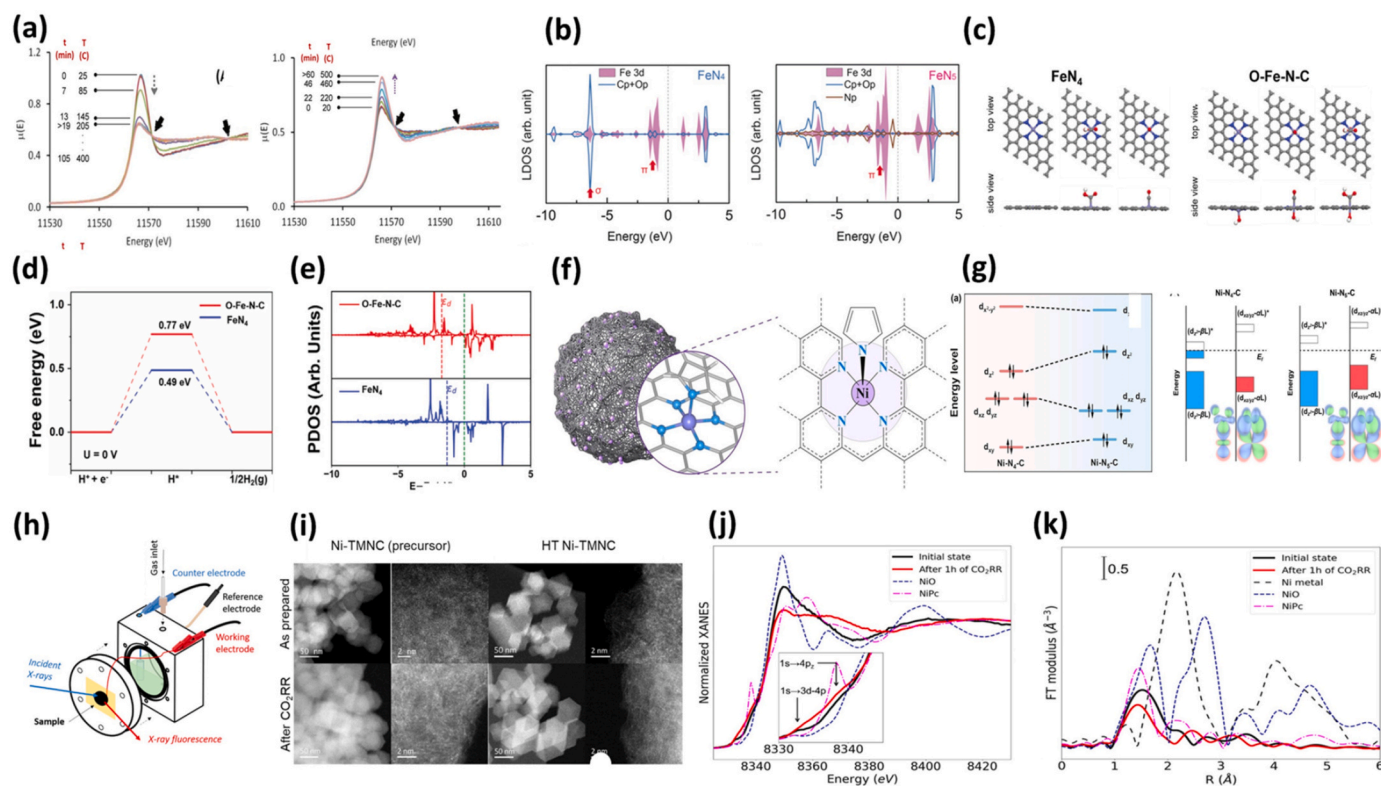


Fig. 7. (a) Time-resolved XANES spectra of air-calcinated Pt-CHA-2 at 500 °C with temperature from 25 to 400 °C (10 °C min⁻¹, 4% H₂) (left panel); Corresponding XANES spectra of Pt-CHA-2 (previously reduced in H₂ at 400 °C) with temperature from 25 to 500 °C (10 °C min⁻¹, 20% O₂) (right panel). Reproduced with permission from Ref. [118] Copyright 2016, Journal of the American Chemical Society. (b) Local density of states of FeN₄ and FeN₅. Reproduced with permission from Ref. [121] Copyright 2019, John Wiley and Sons. (c) Adsorption configuration of FeN₄ and O-Fe-N-C, (d) Energy profile for HER at (0 V vs RHE), and (e) projected density states of FeN₄ and O-Fe-N-C system. Reproduced with permission from Ref. [122] Copyright 2022, John Wiley and Sons. (f) Ni-N₅-C single-atom nanoenzyme and (g) Orbital interaction in CO₂RR and orbital interaction between Ni metal in Ni-N₄-C and Ni-N₅-C system. Reproduced with permission from Ref. [124] Copyright 2022, John Wiley and Sons. (h) Scheme of operando electrochemical cell used for in-situ XAS characterization during the CO₂RR. (i) High-resolution annular dark field imaging of nickel-nitrogen-doped carbon catalysts. (j) XANES and (k) EXAFS spectra collected before and at the end (after 1 h) of the CO₂RR for the HT Ni-TMNC sample. Reproduced with permission from Ref. [125] Copyright 2016, Journal of the American Chemical Society.

EXAFS), which reveals reaction-induced changes in bond length, coordination number, and bond order by monitoring oxidation state and local structure. For example, reversible transformation between the Pt nanoparticles and Pt single atoms in Pt-siliceous chabazite was tracked with XANES and EXAFS. Fig. 7(a) shows XANES analysis elucidated the oxidation state evolution during redox treatments, with decreasing white line intensity (initial spectrum of XANES) indicating H₂-induced reduction (left panel) to metallic Pt⁰ nanoparticles (onset <100 °C, complete ~150 °C, matching Pt foil) and increasing intensity signifying O₂-driven oxidation (right panel) to single Pt atoms (steady at 500 °C), evidenced by well-defined isosbestic points for stoichiometric transitions. This provides the quantitative redox stoichiometry essential for durable single-atom catalysis. Further, in contrast, EXFAS provided a detailed quantitative local structure of post-oxidation and reduction. Pt-Pt bonds at 2.74 Å with a coordination number of ~6-7 confirmed Pt nanoparticles (~1.2-1.5 nm) in the post-reduction, and while post-oxidation shows the absence of Pt-Pt scattering and Pt-O at 2.01 Å with a coordination number of ~3 verified atomic redispersion [118, 119]. Similarly, Rh single atom aggregates into nanoparticles, and it is detected by the Rh-Rh EXAFS signal. Further, under the water-gas-shift half-reaction reverse condition, Rh redisperses back into single-atom sites. When the single atom was treated with H₂, it forms clusters, and further treatment with O₂, the clusters redisperse back into single atoms [120]. Axial ligands downshift the metal d-band center like more negative relative to the Fermi level, weakening H adsorption, often +0.4 to +0.8 eV vs near-zero in planar sites and raising the HER energy barrier, while simultaneously optimizing *COOH formation and facilitating *CO desorption by reducing back-donation to *CO antibonding orbitals. This break scaling relations between *COOH, and *CO, favoring selective CO₂RR over HER and enabling high FE_{CO} (>95–100%) over wide potentials, as evidenced in Fe-N₅, Fe-N₄-O, and Ni-N₅ systems. Zhang et al. investigated Fe-N₅ SAC on N-doped graphene, where one nitrogen atom acts as an axial coordination heteroatom that forms π -coordination covalent bond with the central metal atom by donating electrons. In Fe-N₄, Fe has more d-orbital electrons that back donate to CO. This condition ensures strong binding of the CO product and slows the rate of reaction. From the local density state (Fig. 7(b)), it is clear that compared to Fe-N₄, Fe-N₅ has an additional axial pyrrolic N, which pulls the electron away and raises the Fe valence state. Hence, there is no Fe→CO back donation, and CO can desorb easily. This highlights that the axial N atom stabilizes the isolated Fe atom and tunes the electronic configuration of the active site [121]. The dynamic π -coordination covalent bonding increases the electron density, which enhances the metal ligand interaction by conjugation (delocalization), making the metal atom more stable and immobilizable. Further, replacing the axial N atom with O atom not only helps in the central metal stabilization but also speeds up the reaction kinetics. Zhang et al. constructed Fe-N₄-O SACs (Fig. 7(c)) and proved that Fe-N₄-O has more active sites than Fe-N₄. Fe-N₄-O shows 95% of FE_{CO} at low applied potential (−0.5 V vs RHE). Fig. 7(d) shows HER free energy profiles that conclude Fe-N₄-O (0.77eV) has a higher energy barrier for *H intermediate and allows the electrons to form CO₂ reduction. The projected density of states analysis (Fig. 7(e)) confirms that the axial O atom shifts the Fe 3 d band center to lower energy and weakens the CO adsorption on Fe-N₄-O. This facilitates the faster kinetics of CO desorption and improves the CO₂-to-CO performance [122]. Although in Fe single atom, the axial O atom suppresses HER more than the axial N atom. Chen et al. have compared the CO₂ reduction performance of Fe₁-N₄-O₁ and Fe₁-N₄-N₁. The analysis reveals that the axial O atom shifts the Fe-3d orbital to a lower energy level in the d band center by the O coupling effect. It reduces occupation of antibonding states and further modifies the binding nature of CO₂ reduction. From crystal orbital Hamilton population analysis, it has been confirmed that Fe₁-N₄-O₁ exhibits less integrated Fe-C interaction than Fe₁-N₄-N₁, indicating easier CO desorption. The Fe₁-N₄-O₁ sites decrease the energy barrier for CO₂ reduction and increase the barrier for hydrogen evolution, resulting in higher CO selectivity over a wide

potential window. The Fe₁-N₄-O₁ active site provides 100% FE_{CO} and Fe₁-N₄-N₁ and N doped carbon provides 64% and 27%. Moreover, at −0.83 V, Fe₁-N₄-O₁ delivers current density of 10.23 mA cm^{−2}, which is 2.83 times higher than Fe₁-N₄-N₁ (3.61 mA cm^{−2}). These findings establish an atomic-scale design strategy for single-atom catalysts with a tunable coordination environment, offering stable isolated atom and selectivity for CO₂ reduction [123]. Using similar axial approach, Huang et al. synthesized the single-atom nanoenzyme Ni-N₅-C configuration (Fig. 7(f)). The axial N atom forms square-pyramidal (Fig. 7(g)), Ni-N₅ structure modulates the Ni 3 d orbital energy levels raising the d(z²) orbital and lowering the d(xy/yz)² orbital. The enhance the CO₂ adsorption and CO desorption. Ni-N₅-C delivers FE_{CO} of 97% over a wide potential (−0.8v to −2.4 v vs RHE). At −2.4 V, the catalyst achieves a high CO partial current density of 1.23 A cm^{−2} and TOF of 69.7 s^{−1}. This shows ultra-high current density compared to Ni-N₄-C (>600 mA cm^{−2} and >95%). Hence, the axial coordination shows a significant dual function of stable anchoring of a single atom and CO₂ reduction [124]. Beyond nitrogen and oxygen, other heteroatoms (S, Cl, Br, and I) have also been employed as axial halogen coordinates. Due to the electro-negative properties of the halogens, it modulates the electronic structure by downshifting the Fe 3 d band and weakens the Fe-CO interactions as well as facilitates the CO desorption and avoids the metal aggregation. For example, Fe₂₀-N₄C-Br_{0.3} catalyst achieves 93.78% FE_{CO}, which is 7% higher compared to Fe-N₄C [126]. Hence, the axial coordination facilitates a decisive electronic structure for reinforcing metal atom stabilization and strongly suppresses HER as well as promotes the CO desorption. Compared to all strategies, axial coordination addresses the key limitation in planar strategies and provides incremental improvement in CO₂ reduction performance. Following the optimization in the electronic geometry of SACs, the choice of metal as single atom is essential for developing scalable Zn-CO₂ batteries.

4.5. Scalability: Non-noble metal-based SACs

The employment of the base metals as SACs is a remarkable progress toward large-scale and green energy storage sources. Transition metals such as nickel, cobalt, and iron have gained focus as promising candidates due to their natural abundance, cost efficiency, and tunable electronic structures. Table 2 represents Fe, Co, Cu, and Ni-based SACs as a replacement for noble metals, and different reported M-N-C catalyst in CO₂ reduction. Pyrolysis method of synthesis is widely used in transition metal SACs, which becomes a highly scalable technique for achieving an atomically dispersed catalyst. Co phthalocyanine (CoPc) catalyst molecularly dispersed on N-doped hollow carbon spheres was synthesized by pyrolysis, yielding 95.68% and a current density of 16.49 mA cm^{−2} (at 760 mV overpotential), where the Co 2p-charge loss served as an activity descriptor for efficient CO₂ activation [127]. Liu et al. developed Fe-SAC with boron and nitrogen co-doping, providing 94% FE_{CO} at −0.7 V vs RHE and ~99% FE_{CO} membrane electrode assembly [128]. Through the electrospinning method followed by carbonization, undercoordinated Ni-N₃ sites neighbouring nitrogen dopant were synthesized and achieved 96.6% FE_{CO} with a lower onset potential of −0.3 V for CO₂RR [129]. Zheng et al. Cu-N₂/GN (copper coordinated with two nitrogen sites anchored in graphene) achieved 81% FE_{CO} at −0.50 V due to its unsaturated Cu-N₂ coordination and high atomic dispersion, leading to a Zn-CO₂ battery with a 0.6 mW cm^{−2} peak power density [130]. Cu is the only single-metal catalyst that has the capability to provide C₂₊ products (ethene and ethanol). It is due to the moderate binding affinity, with the intermediate of CO*, which is optimal for C-C coupling [131]. Among all the transition metal SACs, Ni and Fe atoms performs high FE_{CO} and Cu single atom provides valuable liquid C₂₊ products, which are highly used as chemical feedstock and fuels.

A critical comparison of the M-N-C single-atom catalysts reveals clear trends in performance evaluation over different transition metal (TM) atoms in governing CO₂RR selectivity and kinetics, as consolidated in Table 2. Among these Ni-based systems, Ni-N_x-2D/NPC delivers an

Table 2Overview of reported different transition metal and M-N-C based SACs for CO₂RR.

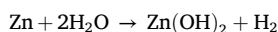
Single TM atom	Catalyst	Method	Catholyte	Product	FE%	BET (m ² g ⁻¹)	Ref
Fe	Fe-N ₄ -O	Hydro-thermal	0.5 M NaHCO ₃	CO	95	-	[122]
Cu	Cu-N ₂ /GN	Pyrolysis	0.1 M KHCO ₃	CO	81	168	[130]
Fe	Fe ₂₀ -N ₄ -C-Br _{0.3}	Pyrolysis	0.5 M KHCO ₃	CO	93.78	1413	[126]
Co	CoPc@DNHCS	Pyrolysis	0.8 M KHCO ₃	CO	95.68	1587	[127]
Fe	Fe-SA/BNC	Pyrolysis	0.8 M KHCO ₃	CO	94	389.2	[128]
Ni	Ni-N ₃ -NCNFs	Electrospinning	0.5 M KHCO ₃	CO	96.6	353	[129]
Ni	Ni-N ₅ -C	Pyrolysis	0.5 M KHCO ₃	CO	97	363	[124]
Ni	Ni-N _x -2D/NPC	Pyrolysis	1 M KHCO ₃	CO	100	1582.9	[132]
Ni	ZrO ₂ @Ni-NC	Pyrolysis	0.5 M KHCO ₃	CO	98.6	469	[133]
Cu	Cu-N-C	Hydro-thermal	0.1M KHCO ₃	CH ₃ COCH ₃	36.7	1565.4	[134]
Fe/Mn	Fe/Mn-N-C	Pyrolysis	0.1M KHCO ₃	CO	94	447.1	[135]
Bi	Bi-N-C	Solvo-thermal	0.1M NaHCO ₃	CO	97	355.4	[136]
Fe	Fe-N-C	Pyrolysis	0.5M KHCO ₃	CO	93.5	-	[137]
Zn	Zn-N _x -C	Pyrolysis	0.5M KHCO ₃	CO	95	1402.7	[138]

outstanding FE_{CO} of 100 % at BET surface area of 1582.9 m² g⁻¹ in 1 M KHCO₃ [132]. The 2D porous structure, combined with modifiable Ni-N_x coordination, specifically low to moderate coordination number and in-plane asymmetry, optimizes stabilization of *COOH intermediate and facilitates CO desorption while suppressing HER. Similarly, ZrO₂@Ni-NC catalyst achieves 98.6% FE_{CO}, demonstrating how an oxide support can further modulate the electronic structure of Ni sites. This highlights the importance of secondary coordination beyond the primary nitrogen ligands, enhancing charge transfer. These Ni catalysts consistently outperform Fe- and Zn-based analogues in selectivity. In contrast, the Cu-N-C catalyst shifts selectivity toward acetone (FE = 36.7 %) despite an exceptionally high BET area of 1565.4 m² g⁻¹ [134]. This underscores the metal-dependent pathway, where Cu favors C-C coupling over CO desorption, a limitation that cannot be overcome by surface area alone and highlights why Cu is less suitable for CO-selective Zn-CO₂ batteries. The bimetallic Fe/Mn-N-C achieves 94 % FE_{CO} [135], demonstrating synergistic electronic modulation between two transition metals, yet still trails optimized Ni systems.

The Fe-N-C catalyst achieves a lower FE_{CO} of 93.5% [137], typical for symmetric Fe-N₄ sites that tend to bind *CO too strongly and allow for minor HER competition. In contrast, Zn-N_x-C demonstrates a competitive FE_{CO} of 95%, paired with BET surface area of 1402.7 m² g⁻¹ [138]. Due to its zinc central metal, this catalyst is uniquely advantageous for Zn-CO₂ batteries as it effectively eliminates the risk of cross-contamination with zinc anode and maintaining superior cathodic efficiency.

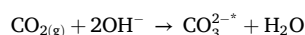
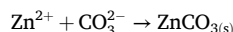
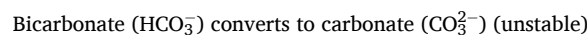
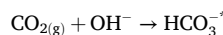
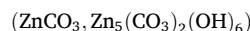
5. Performance of SAC-based cathodes for Zn-CO₂ battery operation

After discussing the basic bottlenecks and tactical improvements of SACs, the most important challenge is how to efficiently introduce them into the Zn-CO₂ battery system. In this section, we critically analyze the main issues and approaches involved in incorporating SACs as high-performance cathode materials for Zn-CO₂ batteries [139]. The performance of Zn-CO₂ battery is based on the ionic conductivity and how well Zn²⁺ interacts with the electrolyte (solvation effects). An efficient battery operation can be obtained by a higher ionic conductivity and a lower charge transfer resistance. When the conductivity is low, there are limited ionic species available that migrate at faster rate and consequently result in large voltage loss that eventually degrades the battery performance. Furthermore, poor ion transport can also lead to uneven Zn deposition and formation of dendrites that are detrimental to the battery performance. In an aqueous system, the zinc anode undergoes self-corrosion



SACs improve homogenized Zn²⁺ flux and planar Zn deposition for

uniform Zn nucleation and avoid dendrites and corrosion. Solvation effects refer to the interactions of Zn²⁺ ions with the neighbouring electrolyte molecules. If Zn²⁺ ions are too tightly bound to the water molecules, they may not be free for reaction and thus will decrease battery performance. Conversely, the bonding is too weak with a risk of side reactions. Due to the stable anchoring structure of SACs, it organizes the water molecule by interfacial water restructuring and reduces the water activity near the Zn surface. Constructive engineering is the most direct and effective strategy to enhance catalytic activity, especially by assembling phase components with different work functions at heterointerfaces, particularly for OER. Zhao et al. reported a CeO₂-CoP nanoneedle array catalyst loaded on Ti mesh (CeO₂-CoP/TM) with work-function (WF) induced directional charge transport properties. By assembling phase components with differing work functions such as CeO₂ (WF ~3.70 eV) and CoP (WF ~4.68 eV) at heterointerfaces, a built-in electric field forms spontaneously, driving directional charge migration from low to high WF regions and facilitating charge spillover to optimize the d-band center, balance electronic density, and accelerate water dissociation kinetics and promotes facile charge spillover, thereby improving the overall electrocatalytic efficiency [140]. SACs act as interfacial regulators and mitigate self-discharge caused by the Zn corrosion. Moreover, introducing additive compounds to the electrolyte would allow tuning solvation properties, inhibit side reactions, and guarantee uniform Zn plating [141,142]. The Zn carbonate precipitate is produced by the formation of intermediates such as bicarbonate (HCO₃⁻) and carbonate (CO₃²⁻), which blocks the cathode surface.



These hydroxides consume CO₂ without forming valuable products. The battery performance and utilization can be improved by using isolated SAC atoms that shift electrons toward CO₂ reduction rather than absorption [143,144]. SAC cathode performance can be profoundly influenced by Potassium bicarbonate (0.1-1.0 M) as it is the standard aqueous electrolyte used. Higher concentrations increase the conductivity and CO₂ availability, enhancing the partial current density for CO production via bicarbonate-assisted proton transfer that stabilizes *COOH intermediates and lowers the overpotentials. The formation of

insulating $\text{ZnCO}_3/\text{Zn}_5(\text{CO}_3)_2(\text{OH})_6$ precipitates raises the resistance and shortens the cycle life due to the elevation in KHCO_3 , which accelerates the local alkalization ($\text{pH} > 10$), rapid $\text{HCO}_3^-/\text{CO}_3^{2-}$ formation, site blocking, and carbonate crossover to the Zn anode. SAC-electrolyte interface can modulate catalysis composition-dependently by the solvation effects. Bicarbonate ions and K^+ cations restructure water layers around metal centers, weakening Zn^{2+} solvation shells while stabilizing CO_2RR intermediates via electrostatic crowding and H-bonding. This results in a shift of equilibria unfavourably by favouring CO selectivity over HER/carbonate formation. K^+ outperforms Na^+/Li^+ for $^*\text{COOH}$ stabilization (lower onset potentials, higher FEs), while anion choice (HCO_3^- vs. $\text{SO}_4^{2-}/\text{Cl}^-$) tunes proton kinetics and SAC durability. An extended life span with a sustained high CO selectivity is obtained by the use of a separated catholyte/anolytes, either KHCO_3 at SAC cathode + KOH at Zn anode or bipolar membranes suppress carbonate crossover, optimize local pH for SAC activity, and preserve uniform Zn^{2+} flux. Despite these advances, systematic progress relating the electrolyte composition, cation/anion effects, and additives offering a long-term SAC performance under realistic cycling remains limited, a critical gap for practical rechargeable Zn-CO_2 batteries [145–147].

5.1. Assessment criteria and evaluation

Current density, overpotential, faradaic efficiency, selectivity, stability, energy efficiency and cell voltage are considered to be the performance metrics of Zn-CO_2 batteries using SACs. A key performance of CO_2RR is a greater current density achieved at a lower overpotential. The benchmark conventional catalysts, bulk metals or metal oxides can be used for evaluation of SAC-based cathodes, which allows for quantifying the edge. SACs are commonly prepared to increase selectivity in a reaction, compared with polycrystalline metal electrodes. However, attaining long-term operational stability remains a major challenge for practical applications.

5.1.1. Material degradation factors and their mitigations

One of the key stability issues involves the deactivation mechanism of SAC under electrochemical conditions. SACs deactivate through a combination of metal-site leaching, support degradation, or coordination-environment collapse, which collectively affect the stability and performance of CO_2RR . The adsorption of hydrogen under the positive potential, at the metal active center or in metal-support coordination sites, will weaken the metal-ligand bonds, and it will promote the detachment of SAC. This is seen in M-N_4 SACs, which govern the tendency for metal leaching during CO_2RR [148]. Over-extended operation of the battery, the practical life time of the cathode is being affected by the long-term deactivation of SACs, which is dominated by metal dissolution, carbon corrosion or support degradation, and active-site poisoning or restructuring. Among all of these, metal dissolution is a main degradation pathway, where atomically dispersed metal centers are oxidized and released into the electrolyte. The presence of unstable isolated atoms will also promote this migration and aggregation into less active clusters. During the electrochemical CO_2 reduction process, isolated metal atoms, such as Fe-N_4 or Co-N_4 , with higher surface energy will leach into the electrolyte or migrate, resulting in the formation of clusters under realistic potentials, extreme pH and attack by reactive oxygen species. High-coordination $\text{M-N}_x\text{-C}$ motifs, dual-atom or multi-atom sites with higher binding energies, and defect-engineered supports that act as deep traps for single atoms, combined with judicious selection of metals and operating windows, will minimise the leaching. These strategies, therefore, focus on strengthening metal-support interactions [149–152]. The second critical degradation factor for many SACs is Carbon corrosion of the support. By the use of high anodic potentials in the presence of radicals, the carbon matrix and N ligands will be oxidized, resulting in the breaking of M-N bonds and exposing the metal center for dissolution. The loss of $\text{Fe}(\text{Co})\text{-N}_4$ sites with carbon oxidation and nitrogen depletion is correlated with fuel-cell durability

studies, whereas in corrosive media like seawater, aggressive anions and fluctuating conditions will further accelerate this support degradation. Recent works have been focused on robust supports, such as graphitised carbons, doped carbons, conductive carbides/nitrides, and corrosion-resistant oxides such as TiO_2 or CeO_2 , often combined with protective but conductive shells that shield the core support without blocking access to single-atom sites. Strong absorbing species such as sulfur, halides, CO, or organic impurities can block the sites or alter the local coordination environment, as SACs are also most vulnerable to poisoning effects. This can be overcome by customising the coordination environment and second-shell chemistry to reduce binding of poisons compared to the binding of desired reactants, and by developing corrosion-resistant SACs with metal-support bonding and local electronic structures that prevent halide adsorption. Additional measures include electrolyte purification and using sacrificial scavengers for harmful anions or radicals based on the compatibility of the application [153–155].

Further to directly assess the stability of the metal centers themselves, such as detachment and aggregation, operando characterization techniques are employed to monitor the evolution of single-atom sites under electrochemical conditions. Continuous redox cycling and carbon support oxidation lead to structural modification in the single-atom surrounding. This promotes the aggregation of isolated atoms to nanoparticles and modifies product selectivity. Hence, the stability of the single atom is confirmed by the operando XAS, which acts as a specialized probe that identifies the chemical state and physical arrangement of metal atoms (Fig. 7(h)) [125,156]. The data display the specific active moieties responsible for driving CO_2RR . In particular, XANES is the best way to find the active part of the catalyst. For example, a single Ni atom transition metal was synthesized with ZIF-8 precursor at high temperature with N-doped carbon (HT-Ni-TMNC). The presence of an individual Ni atom is confirmed with the HAADF-STEM (Fig. 7(i)) by the clear rhomboid-dodecahedron morphology of N-doped carbon and no formation of Ni nanoparticles. In Fig. 7(j), the Ni-edge absorption position agrees with reference materials containing Ni in the +2-oxidation state. Initially, the XANES spectrum shows a strong white line peak at 8350 eV similar to NiO but broader, and additionally two smaller pre-edge peaks at 8333 eV and 8338 eV. Under CO_2RR , the white line becomes weaker, while the two pre-edge peaks get stronger. These pre-edge features are known to come from a planar Ni complex; the stronger one at 8338 eV is square-planar Ni-N_4 with D_{4h} symmetry. When that peak weakens, the square geometry becomes distorted, and the other pre-edge peak becomes more intense. Hence, Ni oxidation state remains +2 (there is no edge position shift) and there is no metallic Ni. The metal Ni remains single-atom but reconstructs from octahedral Ni^{2+} into a distorted square-planar Ni-N_4 structure. Fig. 7(k) shows Fourier-transformed (FT) EXAFS, where a peak at 1.5 Å refers to the octahedral Ni coordination, similar to NiO, with no clear peaks for Ni-Ni nanoparticle, confirming single-atom dispersion. During CO_2RR , the main peak gets weaker, the surrounding peaks get stronger, indicating rearrangement of the Ni-N and Ni-C environment. All peaks shift to a shorter distance, which explains the shorter distance of Ni-N and Ni-C, indicating that the Ni atom remains isolated without aggregation. The presence of any nanoparticle can be easily detected using XANES and FT-EXAFS. Similarly, Martini et al. synthesized Co-N_4 with two axial oxygen ligands. Unexpectedly, its XANES spectrum is different from pure Ni-N-C species, where a pre-edge peak at lower energy, suggesting a more reduced Co state, and FT-EXAFS shows second-shell contribution at $R \sim 2.27$ Å with k-space feature similar to Co-Co bonds. These results indicated the presence of small Co-Co clusters rather than the isolated single Co atom [125,157]. Operando characterization provides direct evidence that the metal centers in SACs remain atomically dispersed under CO_2RR , while also revealing redox-induced modification of the coordination surroundings rather than nanoparticle formation. By correlating the single-atom configuration with stability and activity, we can interpret the

subsequent electrochemical performance of SACs in Zn-CO₂ batteries.

5.1.2. Electrochemical characterization of SACs in Zn-CO₂ batteries

The catalytic activity of SACs in Zn-CO₂ batteries is governed by CO₂ reduction activity, product selectivity, overpotential, and long-term cycling stability under operating conditions. As mentioned in earlier sections on MOF-derived SACs, the well-ordered structure of MOFs will facilitate precise control over SAC dispersion and uniformity, making them most suitable for catalytic applications. Li et al. reported that Ni-N/OMC-1 as a cathode catalyst for a rechargeable Zn-CO₂ battery, driven by its CO₂RR capabilities. When discharged at a current density of 2.5 mA for Ni-N/OMC-1, which showed CO₂-to-CO conversion, the established FE_{CO} was 92% and its high efficiency was sustained at a wide range of direct current (Fig. 8(a)). Also, HER products were observed, with less than 5% FE (H₂) while discharging. The FE_{CO} of Ni-N/OMC-1 could outperform Ni-N/C by maintaining near 100% over a wide voltage range from -0.2 to -1.1 V (vs. RHE) (Fig. 8(b)). The stability of Ni-N/OMC-1 demonstrated by maintaining performance for over 25 h after 125 cycles of continuous discharge-charge processes at 0.5 mA (Fig. 8(c)) [158]. Sun et al. developed a novel self-supporting nickel single-atom catalyst (Ni-N_x-b/CP) for efficient CO₂RR. The synthesis involved growing a nickel MOF on carbon paper, followed by calcination, which resulted in a three-dimensional hexagonal prism structure with abundant porous sites due to the contribution of 4, 4-bipyridine ligands. Notably, as shown in Fig. 8(d), Ni-N_x-b/CP also exhibited excellent CO selectivity with a FE_{CO} over 90%, and its great charge-discharge performance, reflecting outstanding reversibility (Fig. 8(e)). Moreover, Ni-N_x-b/CP-based Zn-CO₂ batteries could realize a high-power output of 1.10 mW cm⁻² at 3.46 mA cm⁻², which also displays highly durable and cycling-stability performance with only a small, almost-constant difference in charge-discharge curves even after over-cycling for more than 20 h (Fig. 8(f)) [159]. These results talk about the prospects of Ni-N_x-b/CP, and demonstrate that it is a highly active and stable CO₂ reduction electrocatalyst for both electrochemical flow cells and Zn-CO₂ battery systems. Moreover, it is promising to promote other catalysts via the use of a similar strategy to achieve their superior catalytic performance and overcome the drawbacks of nano-scale powder-based single-atom catalysts. Among carbon-based nano-supports, graphene and its derivative materials, carbon nanotubes, as well as other porous carbons, can be designed with SACs to support catalytic centers, allowing the modulation of both conductivity and surface properties. For instance, Chen et al. fabricated a SAC with isolated atomically dispersed Fe-N₄ and Fe₃C nanoparticles (Fe₃C|Fe₁N₄) confined in carbon as efficient CO₂RR and Zn-CO₂ battery electrocatalysts. This catalyst presents a fragmental-rock structured nano-carbon with isolated Fe-N₄ species uniformly dispersed throughout and alongside Fe₃C nanoclusters. The proposed reaction mechanism (Fig. 8(g)) suggests that CO₂ is first adsorbed onto the Fe₃C|Fe₁N₄ active sites, where it undergoes an initial electron transfer to form the *CO₂⁻ intermediate. This intermediate is subsequently protonated, facilitated by a proton donor from H₂O, leading to the formation of *COOH. Further protonation and dehydration of *COOH generate the *CO intermediate, which remains bound to the catalyst surface before eventual desorption. The CO₂ER performance of Fe₃C|Fe₁N₄ was also assessed by the research group in a three-electrode H-cell assessed using a 0.5 M KHCO₃ electrolyte saturated by CO₂. Only H₂ and CO were detected as final gaseous products, with a total FE approaching 100%. Control samples were synthesized by an atomically dispersed Fe₁N₄ catalyst, fully suppressing Fe₃C nanoparticle formation, a bare Fe₃C catalyst was obtained by preventing Fe₁N₄ formation. In addition, an Fe-free nitrogen-doped carbon catalyst was used to evaluate CO₂ER performance. A negligible CO₂ER activity was exhibited by the bare Fe₃C catalyst. The FE_{CO} of NC remained below 24% across all applied potentials (Fig. 8(h)). Whereas, Fe₁N₄ and Fe₃C|Fe₁N₄ catalysts exhibited a significantly higher CO selectivity, FE_{CO} of 94.3% and 94.6% at -0.5 V, respectively. Furthermore, Fe₃C|Fe₁N₄ outperformed Fe₁N₄ (4.7 mA cm⁻²) and NC (1.7 mA

cm⁻²) by delivering a current density of 6.4 mA cm⁻² at -1.0 V at the same potential. When compared with other CO₂ER electrocatalysts (Fig. 8(i)), including Fe-N-C and carbon-supported nonprecious metal nanoparticles, Fe₃C|Fe₁N₄ displayed superior CO₂ER activity, achieving higher FE_{CO} at a given applied potential. Capitalising on its outstanding CO₂ER activity, the Fe₃C|Fe₁N₄ was considered as a cathode material in a rechargeable Zn-CO₂ battery (Fig. 8(j)). The electrochemical performance of the Fe₃C|Fe₁N₄-based Zn-CO₂ batteries was using discharge and charge polarisation curves (Fig. 8(k)), revealing a high-power density of 0.33 mW cm⁻². The voltage plateaus remained stable across varied current densities (0.5 to 1.5 mA cm⁻²) (Fig. 8(l)), demonstrating robust operational performance. Long-term cycling tests confirmed excellent rechargeable durability, with a constant voltage profile at 0.5 mA cm⁻² over 40 h (110 cycles) of continuous charge-discharge operation [160].

In the Zn-CO₂ batteries, CO₂ transport in the gas diffusion electrode (GDE) is commonly employed for controlling both liquid electrolytes and gas products. SACs are assembled in the porous GDE structure and facilitate the gas-liquid-solid three-phase interface during CO₂ reduction. Wang et al. adopted a gas-diffusion combined with pyrolysis method for preparing N-doped porous carbon polyhedra containing atomic Fe sites. The resulting catalyst, designated Fe₁NC/S₁-1000, exhibited exceptional CO₂ER activity, achieving a FE_{CO} of 96% at -0.5 V and a TOF of 2225 h⁻¹. With the exceptional CO₂ER performance of Fe₁NC/S₁-1000, it was used directly as a cathode material in a rechargeable Zn-CO₂ battery. The battery utilized 0.8 M KOH with 0.02 M Zn (CH₃COO)₂ as the anodic electrolyte and 0.8 M CO₂-saturated KHCO₃ as the neutral cathodic electrolyte. During discharge, CO₂ER occurred at the cathode, while Zn dissolution took place at the anode [161].

Upon discharge, the applied potential could stimulate OER on the cathode, and Zn²⁺ reduction to metallic Zn at the anode. Zn-CO₂ Battery of the type Fe₁NC/S₁-1000 was characterized by OCV value of 0.727 V, which is in good accordance with the theoretical electromotive force value + 0.707 V, which represented only partial inhibition of hydrogen evolution through CO₂ER catalysis. Discharge and charge polarisation curves (Fig. 8(m)) indicated that Fe₁NC/S₁-1000 cathode delivered a current density of 52 mW cm⁻², significantly higher when compared to 97 mW cm⁻² reported for NC/S₁-1000 cathodic catalyst. Furthermore, Zn-CO₂ battery fabricated from Fe₁NC/S₁-1000 showed outstanding rechargeability with a reversible charge-discharge voltage gap (~0.5 V over 72 cycles (25 h)) at 0.5 mA cm⁻² (Fig. 8(n)) [161]. The improved performance of Fe₁NC/S₁-1000 could be due to the increased ECSA and optimized active center with an increased accessible and intrinsic activity for iron sites. Both experimental and theoretical results indicate that the Fe-N₃ moieties in Fe₁NC/S₁-1000 possess simultaneous *COOH and *CO intermediate adsorption energies, which is crucial for proficient production of CO. The adaptability of this gas-diffusion approach for the fabrication of dimension-controlled carbon-supported SAC with Fe atoms means that this method opens new avenues in energy storage and conversion. Besides the conventional planar geometry, the introduction of axial heteroatoms has been explored in CO₂RR and it emerged as an underexplored design principle for Zn-CO₂ batteries. A lower energy barrier for *COOH formation can be obtained by axial heteroatoms such as N, O, and Cl, which facilitates CO desorption, resulting in enhanced CO selectivity and reduced HER activity. For instance, asymmetrically coordinated Sn-N₃O₁ and Fe-N₄-O active sites exhibit dramatically improved CO faradaic efficiencies compared to their symmetric M - N₄ counterparts, highlighting the decisive role of axial ligands in governing reaction pathways [162,163]. Therefore, developing robust strategies of stable axial-ligand-modified single-atom active sites is critical for advancing next-generation electrocatalysts with superior activity, selectivity, and durability for Zn-CO₂ batteries.

The introduction of an axial nitrogen ligand to create Fe-N₅ sites has been shown to significantly enhance the catalytic performance of both

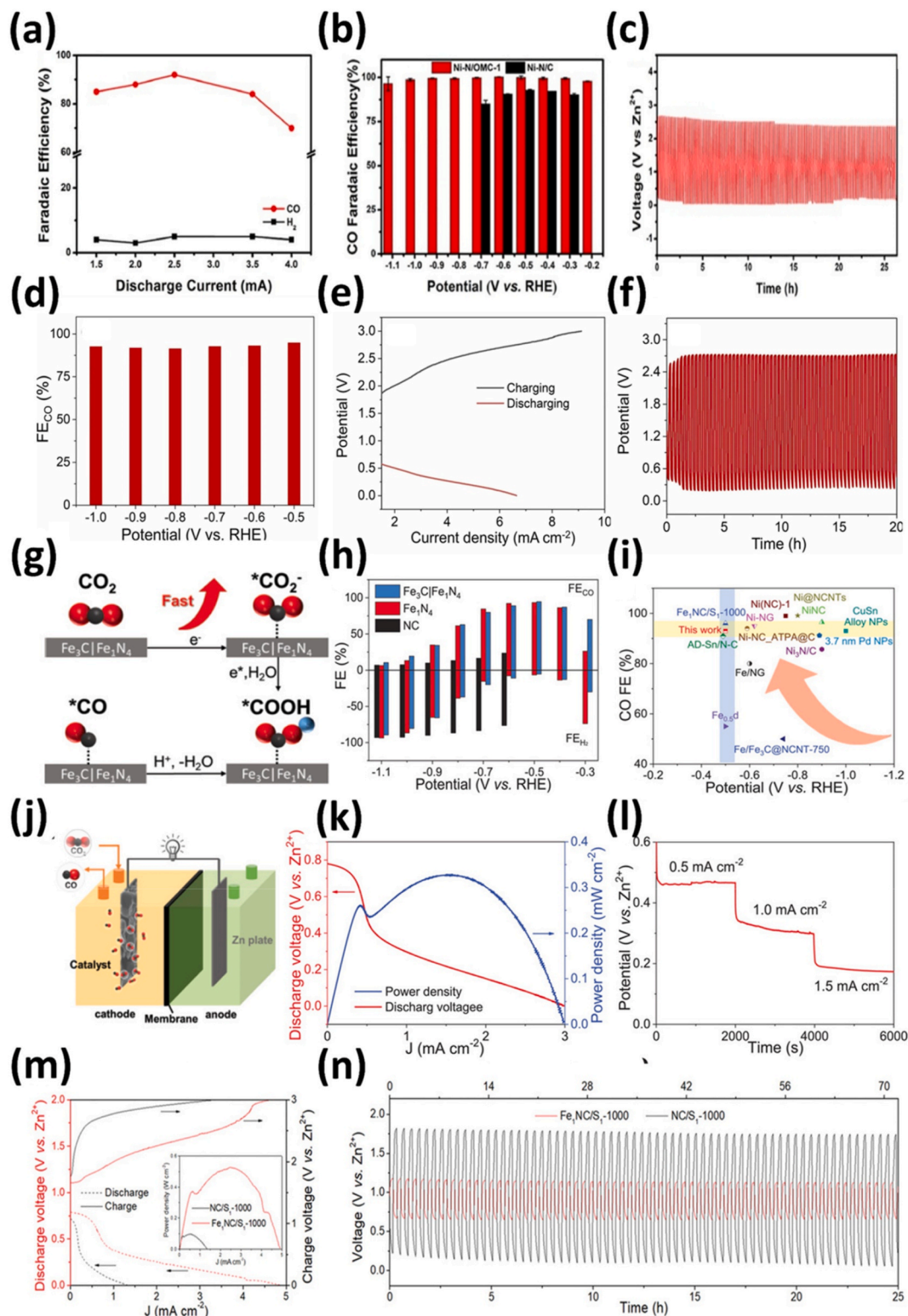


Fig. 8. (a) FE under different discharge currents for CO and H₂, (b) FE_{CO}, (c) galvanostatic discharge-charge cycling curves at 0.5 mA, with a stable voltage during 125 cycles. Reproduced with permission from Ref. [158] Copyright 2022, Springer. (d) FE_{CO} at different potentials, (e) Charging and discharging curves, (f) Cyclic stability of Ni-N_x-b/CP based Zn-CO₂ battery for 20 h. Reproduced with permission from Ref. [159] Copyright 2025, Elsevier. (g) Reaction pathway of CO₂ER on Fe₃C|Fe₁N₄, (h) FE_{CO} of NC, Fe₁N₄, and Fe₃C|Fe₁N₄, (i) Comparison of FE_{CO} of Fe₃C|Fe₁N₄ with other representative Fe-N-C and carbon-supported non-precious metal NPs catalysts, (j) Schematics of a rechargeable Zn-CO₂ battery based on Fe₃C|Fe₁N₄ cathode. (k) Polarisation and power density plot of Fe₃C|Fe₁N₄ cathode-based Zn-CO₂ batteries, (l) Galvanostatic discharge curve for various current densities. Reproduced with permission from Ref. [160] Copyright 2022, John Wiley and Sons. (m) Polarisation and power density plots, and (n) galvanostatic discharge-charge cycling plots at 0.5 mA cm⁻² for 72 cycles of Fe₁NC/S₁-1000 and NC/S₁-1000-based Zn-CO₂ batteries. Reproduced with permission from Ref. [161] Copyright 2020, John Wiley and Sons.

the electrochemical CO₂ reduction reaction and Zn-CO₂ battery applications. The FeN₅ catalyst, supported on defect-rich nitrogen-doped carbon (FeN₅@DNC), was tested in various electrochemical setups. The FeN₅@DNC catalyst is used as a cathode for a reversible Zn-CO₂ battery. The assembled battery exhibited a power density of 0.6 mW cm⁻² at a current density of 1.6 mA cm⁻², while maintaining 90% FE_{CO} at various current densities [164]. The axial coordinated nitrogen plays a crucial role in the discharge polarisation and enhances the corresponding power density in Zn-CO₂ battery. Further, Chen et al. reported that bringing an axial oxygen ligand into the conventional planar Fe-N₄ coordination generates an asymmetric Fe-N₄O active site, which thereby enhances the CO₂ electroreduction performance. The Fe-N₄O-C nanoplates covalently bonded to graphene ensure uniform dispersion of Fe single atoms, while axial O coordination significantly modifies the electronic structure of the Fe center. The charge-discharge polarisation curves with corresponding power density of 0.96 mW cm⁻² at the current density of 4.0 mA cm⁻². The cycle stability was maintained for 74 h at a current density of 1.0 mA cm⁻². Moreover, CO product is delivered across a current density of 1-7 mA cm⁻² with a maximum FE_{CO} of 90.1% at 3.0 mA cm⁻² over a wide voltage window and superior intrinsic activity compared with Fe-N₄ sites without axial coordination, highlighting axial ligand engineering as an effective strategy for tuning active-site reactivity in single-atom catalysts [165]. Peng et al. demonstrated that introducing an axially coordinated halogen atom (Cl, Br, or I) into planar Ni-N₄ single-atom sites effectively breaks the symmetry of the Ni centers' electronic structure and enables precise regulation of their electronic states. While using Ni₁-N-C (Cl), the selectivity of CO is 93.8 % at 2 mA, showing its CO₂ reduction performance. DFT results show that the electronegative Cl reduces the activation energy barrier for *COOH and shortens the distance between absorbed *COOH and the Ni atom. Even under continuous charge/discharge for 24 h at 2 mA cm⁻² shows its excellent stability [166]. These results conclude that the introduction of an axial ligand exhibits effective tuning in lowering the activation energy barrier in Zn-CO₂ batteries. Therefore, recent advances demonstrate that axial coordination can bridge the performance gap between CO₂RR and Zn-CO₂ battery conversion. But still, the axial coordination engineering strategies in SACs for Zn-CO₂ batteries are in an early developmental stage.

5.2. Benchmarking against conventional catalysts

The performance of SACs in the Zn-CO₂ electrochemical system is compared with that of traditional bulk metals and metal oxides using fundamental electrochemical parameters. A very important parameter is the current density, and SACs exhibit current densities of 10-50 mA cm⁻² that are much higher when compared to bulk metals (5-20 mA cm⁻²) and metal oxides (1-10 mA cm⁻²). This promotion of current densities is due to the distribution of active sites in SACs, which permits better CO₂RR kinetics. Overpotential, another key factor, in which the SACs work at ≤0.5 V is much lower than both the bulk metals (0.6-1.0 V) and metal oxides (0.7-1.2 V) [167,168].

In addition, the specificity for desired products of CO₂ reduction (CO or formate) is orders of magnitude superior in SACs to that in bulk metals and metal oxides, as they typically co-produce a mixture of CO, H₂, and hydrocarbons. For example, Fe-based SACs show >95% selectivity for CO generation, in contrast to Cu-based bulk catalysts, which give rise to several products at lower efficiency [142]. Stability is also an important performance parameter of SACs (several tens of hours) with only minimal decrease, which is much better than that of bulk metals (50-70 h) and metal oxides (20-50 h). This stability is obtained by the strong interaction among the individual metal atoms and the support matrix, suppressing both aggregation and deactivation processes. Besides, the energy efficiency of the SAC-based Zn-CO₂ batteries is higher than 80%, which is better than that for bulk metals (50-70%) and metal oxides (50-75%). SACs can also be operated at 2.0-2.5 V, indicating its higher electrochemical performance in the Zn-CO₂ battery. In general,

the durable activity, selectivity, and stability of SACs combined with CO₂RR support the highly promising application of SACs as catalysts for Zn-CO₂ batteries. Their atomic dispersity leads to high utilization of active sites and reduced overpotential, lowering energy loss as well [169]. Moreover, different non-noble metal catalysts are presented and compared in Table 3, each demonstrating specific and favourable Zn-CO₂ performance metrics. In non-noble metal catalysts, Fe-doped perovskite and SnLi retain stability for 80 h and 85 h at the current density of 1 mA cm⁻² and 0.5 mA cm⁻² [170,171]. These findings underscore the strong stability of leading non-noble catalysts.

Benchmark metals like Au and Ag facilitate CO₂ reduction with a high selectivity and activity toward CO at lower overpotential. These materials were referred for evaluating newly developed catalysts in Zn-CO₂ batteries. Table 4 compares the key electrochemical parameters of the benchmark catalysts, noble metal catalysts, and different SACs in Zn-CO₂ batteries. Ko et al. achieved a maximum power density of 7.89 mW cm⁻² and 5.52 mW cm⁻² with Au and Ag catalysts in a CO₂-injected system, and obtained FE_{CO} of 92.72% for Au and 89.56% Ag [185]. Further, AgAs/CC attributes its own peculiarity to be implemented with a FE_{CO} of 95.3% and power density at 2.16 mW cm⁻². The fabricated Zn-CO₂ battery ran continuously for 50 h at a current density of 3 mA cm⁻² [186]. Noble metal catalyst like BiPdC cathode in the Zn-CO₂ battery delivers a peak power density of 0.42 mW cm⁻², and FE_{HCOOH} up to 52.64% across discharge currents [187]. However, in Zn-CO₂ batteries, the requirement for product selectivity, stability, and cost efficiency makes benchmark catalysts and single-atom catalysts more competitive. Among the different types of SACs, it has been demonstrated that Ni SAC shows superior faradaic efficiency and long-term stability. Ni-N₃-NCNFs and Ni-N_x-2D/NPC exhibit a continuous operation for 46 and 50 h at the current density of 2 mA cm⁻² and 0.5 mA cm⁻² [129,131]. Further axially coordinated Fe single atom (Fe-N₄O-C) delivers a power density of 0.96 mW cm⁻² with durable cyclic stability of 72 h at 1 mA cm⁻² [165]. While benchmark catalysts (Au and Ag) dominate in power density, SACs (Ni and Fe) stand out for their cost-effectiveness, FE, extended stability, and overall viability for scalable Zn-CO₂ batteries.

Beyond the established non-noble composite materials, benchmark catalysts, and noble metal catalysts, single-atom catalysts make a distinct contribution by providing high selectivity and electrochemical performance with minimal metal loading. The development of dual single-atom catalysts (DSAC) is also an emerging arena for enhanced catalytic activity. DSAC provides two different metal sites, which optimize the absorption sites of the catalytic path on the support, and lead to increased concentration of metals with a greater density of active sites.

DSAC resolves the limitation of linear scaling for reactivity intermediates and leads to enhanced catalytic activity in Zn-CO₂ battery via a multi-step pathway [188]. In addition, without using a double-compartment electrolyte, the rocking chair Zn-CO₂ battery can be expanded to an aqueous electrolyte system [169]. The adaptation of hydrogel electrolytes prevents the anode to be corroded by water molecules [189]. Although great progress has been achieved, it is highly desirable that these components can be promoted simultaneously, and more in-depth research is needed to realize the full potential of SACs toward high-performance, efficient, durable Zn-CO₂ storage and CO₂ utilization systems.

5.2.1. Consolidated mechanistic framework: From atomic descriptors to Zn-CO₂ performance

Atomic coordination descriptors represent the primary structural parameters such as the coordination number (CN), bond lengths, and the chemical identity of neighbouring ligands, such as N, S, P, O, that define the local environment of a catalytically active site. These descriptors are not just geometric identifiers, but they are the fundamental drivers of the electronic structure for SAC. The local symmetry and electronegativity can be modified by altering the coordination environment, such as substituting a nitrogen atom for a sulfur atom in a M-N-C matrix. This kind of structural "tuning" will shift the d-band center (ϵ_d) of the

Table 3

Comparison of electrochemical parameters with non-noble metals.

Category	Catalyst	Selectivity	FE (%)	Power Density (mW cm ⁻²)	Stability	Cycle Life	OCV	Energy Efficiency (%)	Ref
Non-noble metals	Fe-substituted perovskite	CO	82	1.27	80 h 1 mA cm ⁻²	100	-	-	[170]
	SnLi	HCOOH	-	1.24	85 h 0.5 mA cm ⁻²	>800	-	-	[171]
	Fe-N ₅ /DPCF	CO	90	1.3	25 h 0.5 mA cm ⁻²	75	-	-	[172]
	In/ZnO @CNCs	HCOOH	90	1.32	51 h 1 mA cm ⁻²	153	-	-	[173]
	Sn/NCNFs	CO	97.6	1.38	35 h 0.5 mA cm ⁻²	100	-	-	[174]
	Fe@NPC	CO	90	3.0	40 h 0.5 mA cm ⁻²	120	-	-	[175]
	Zn-N ₃₊₁	CO	95	1.8	26 h 1.5 mA cm ⁻²	100	-	-	[176]
	Ni ₄ N/Ni ₃ ZnCo _{0.7}	CO	68.9	0.85	15 h 0.5 mA cm ⁻²	-	-	-	[177]
	BiC/HCS	HCOOH	96	7.0	65 h 1 mA cm ⁻²	-	-	68.9	[178]
	NiPG	CO	90	1.95	12 h 0.5 mA cm ⁻²	-	1.53	-	[179]
	Bi-D	CO	93.9	1.16	22 h 5 mA cm ⁻²	66	1.3	-	[180]
	s-PdNi/CNFs-1000	CO	96.6	1.95	35 h 1.2 mA cm ⁻²	-	-	-	[181]
	ZnTe/ZnO@C	HCOOH	68	0.93	36 h 1 mA cm ⁻²	108	1.35	-	[182]
	PNCB	HCOOH	80	1.43	20 h 5 mA cm ⁻²	120	-	-	[183]
	Pd NS	HCOOH	90	-	33 h 0.5 mA cm ⁻²	100	0.89	81.2	[184]

Table 4Performance comparison of different SACs with the benchmark catalysts in Zn-CO₂ batteries.

Category	Catalyst	Metal atom	Supportive matrix	Active-site configuration	Selectivity	FE (%)	Power Density (mW cm ⁻²)	Stability	Cycle life	Energy efficiency (%)	Ref
Benchmark Catalysts	Coralloid Au	Au	Carbon paper	Nanoparticles	CO	94.2	0.7	68 h 1 mA cm ⁻²	-	-	[25]
	Au and Ag catalyst	Au and Ag	Carbon paper	Au and Ag nanoparticles	CO	89.56 and 94.02	7.89 and 5.52	10 h 4 mA cm ⁻² and 7.5 h 4 mA cm ⁻²	-	Au-14.98	[185]
	AgAs/CC	Ag	Carbon cloth	Ag nanoparticle	CO	95.3	2.16	50 h 3 mA cm ⁻²	-	59.85	[186]
Noble metal	BiPdC alloy	Pd	Carbon nanosheets	BiPdC	HCOOH	52.6	0.42	45 h 0.5 mA cm ⁻²	-	-	[187]
Co-SAC	CoPc@DNHCS	Co	Nitrogen-doped hollow carbon spheres	Co-Pyrrolic N	CO	94	1.02	40 h 1 mA cm ⁻²	-	-	[127]
Cu-SAC	Cu-N ₂ /GN	Cu	Graphene	Cu-N ₂	CO	64	0.62	40 h 1 mA cm ⁻²	120	-	[130]
Ni-SAC	Ni-N ₃ -NCNFs	Ni	Carbon nanofiber	Ni-N ₃	CO	96	1.05	46 h 2 mA cm ⁻²	140	-	[129]
	Ni-Nx-2D/NPC	Ni	Nitrogen-doped porous carbon	Ni-Nx	CO	95	-	50 h 0.25 mA cm ⁻²	-	-	[131]
	ZrO ₂ @Ni-NC	Ni	Nitrogen-doped porous carbon	Ni-N ₄	CO	>90	-	33 h 1 mA cm ⁻²	100	-	[133]
Fe-SAC	Fe-SA/BNC	Fe	B-N Co-doped carbon	Fe-N ₃ B	CO	94	1.18	30 h 1 mA cm ⁻²	80	66.26	[128]
	Fe ₁ NC/S ₁ -1000	Fe	N-doped porous carbon	Fe-N ₃	CO	96	0.6	25 h 0.5 mA cm ⁻²	75	-	[161]
	FeN ₅ @DNC	Fe	Nitrogen-doped carbon	Fe-N ₅	CO	90	0.6	24 h 0.5 mA cm ⁻²	-	-	[164]
	Fe-N ₄ O-C (Gr)	Fe	Graphene	Fe-N ₄ O	CO	98.03	0.96	72 h 1 mA cm ⁻²	-	-	[165]

transition metal, which determines how strongly the catalyst will bind to reaction intermediates. Based on the arrangements of atoms at the sub-atomic scale, these descriptors can serve as the “blueprints” for material design, allowing researchers to predict catalytic activities. Descriptors play an important role in governing the reaction kinetics and selectivity at the cathode during the electrochemical process in a Zn-CO₂ battery. The coordination environment has a direct influence on the Gibbs free energy (ΔG) of the reaction intermediates, specifically on the formation of *COOH and the subsequent desorption of *CO. By ensuring that the binding energy is neither too strong, which would poison the site, nor too weak, which would fail to activate the CO₂ molecule, by a well-optimized atomic descriptor. These descriptors are further essential for the strategic suppression of the HER. By improving the energy barrier for hydrogen adsorption (ΔG_{H^*}) by altering the specific ligand coordination, the catalyst can “filter” the available protons in the aqueous electrolyte, which ensures that electron transfer is directed exclusively for the CO₂ reduction. A high Faradaic efficiency and a stable discharge voltage in the final system are obtained by this atomic-level control.

The development of high-efficiency aqueous Zn-CO₂ batteries requires a mechanistic framework that can connect between discrete atomic-scale modifications and overall device metrics. This review discusses about a hierarchical causal chain of structural, electronic, and thermodynamic stages to find the final electrochemical output. A local anisotropy is introduced at a primary structural level, specifically by the transition from a symmetric M – N₄ coordination to an asymmetric, heteroatom-doped M – N₃S₁ environment. By this breaking of symmetry, it's not just a geometric shift but a fundamental driver of electronic modulation. Lower electronegative atoms like sulfur will induce a significant shift in the d-band center of the transition metal active site, as shown by the DOS analysis. By maximising the orbital overlap between the metal center and the carbonaceous adsorbates, this electronic signature serves as a predictive description for the catalyst's attraction for reaction species. The intermediate energetics of the competitive reduction routes in the aqueous electrolyte are directly controlled by this electrically adjusted surface. The CO₂ Reduction Reaction can be effectively accelerated by the shift in d-band center which reduces the ΔG barrier for the formation of the critical *COOH intermediate. The strategic suppression of the HER, along with the modified coordination environment, yields significantly more positive ΔG for hydrogen adsorption. This dual-action control over thermodynamics ensures that the catalyst is highly selective toward carbon products and must have high-energy-density systems. Finally, this atomic-level alignment leads to a macroscopic Zn-CO₂ battery performance. By lowering the kinetic (energy barrier) overpotentials, the battery achieves a more stable voltage during discharge and better selectivity leads to higher specific capacities and faradaic efficiencies. Moreover, a coordinated structure ensures cyclic stability and is maintained over long-term durations. By combining these factors into a singular process, this framework provides a “bottom-up” template for designing cathode material, shifting the field from trial- and-error synthesis toward descriptor-based engineering material [190,191].

5.2.2. Balancing mechanistic descriptors with practical trade-off and synthetic complexity

The three levers, including axial linkage, coordination modulation, and defect mediation, each exert unique yet interconnected influences on key catalytic descriptors, with significant differences in magnitude and specific chemical pathway of their effect. The electronic structure of the metal atom is modulated by axial heteroatomic linkage through outer planar ligand field interaction, inducing charge redistribution and changing orbital occupancy (metal d-orbital). Axial linkage shifts the d-band center and modifies the metal-adsorbate coupling, thereby allowing fine regulation of adsorption energies (ΔE_{ads}) of intermediates like *COOH and *CO. The inner planar coordination (e.g., M – N₄ to M – N₃, or asymmetric coordination) introduces substantial changes in local symmetry, coordination unsaturation, and crystal-field splitting, which

simultaneously reshape the electronic structure. The geometric perturbation influences orientation, binding affinity, and the CO₂RR and its intermediates, thereby dictating reaction mechanism and selectivity. At the same time, defect-mediated engineering (e.g., vacancies, edge effect, and heteroatoms-induced distortion) generates highly localized electronic states and low-coordination active sites, which enhance orbital overlap with adsorbates. Compared to axial and coordination states, defect engineering is often the most powerful way to accelerate a reaction and substantially lower ΔG as well as E_a of elementary steps.

Moreover, defect sites decouple conventional scaling relationships, ensuring improved catalytic efficiency besides the intrinsic limitation. Consolidating these three strategies, axial linkage offers electronic tuning without changing the geometric disruption, coordination modulation provides combined control over both electronic and geometry, and defect engineering primarily optimizes the reaction mechanism. This comparative mechanistic framework exhibits a direct structure-descriptor activity relationship, offering critical insights for developing a design of a high-performance catalyst for CO₂ electroreduction [192,193]. Table 5 compares the strategies across key descriptors, indicating distinct trade-offs essential for experimental design. Different metals centers (Fe, Co, Ni, Cu) in SAC for CO₂RR show varying performance due to differences in the filling of the d-band center. In Fe and Co, the selectivity is toward CO products with high defect engineering. The axial coordination of these metals also supports in boosting the key intermediate activity. The hetero-atom coordination support also helps in anchoring and stabilization of single atom. While in Ni and Cu, defect-mediated stabilization support moderates with selectivity of CO and formate. The axial coordination of Ni and Cu has good coupling and assists in the support of HER. Ni and Cu are atomically stable in the heterojunction coordination environment [194,195]. All three engineering strategies to improve SACs in CO₂RR address key points with distinct metals. Defect engineering makes Fe and Co very stable but lowers initial activity. Heterojunctions give good durability for Ni and Cu. While axial coordination environment works for all metals, increase the activity, easy synthesis, and scalability.

5.3. Potential commercialization aspects

Currently, the electroreduction of CO₂ to CO is hindered by big-scale industrial adoption due to slow reaction rates and short-term stability, which makes it difficult for them to be implemented in industry. There are a few commercialization and scale-up issues.

- Cost:** In this regard, the expensive noble metal SACs such as Pd, Ag, Au and Ru restricts their large-scale industrialization despite perfect performance. Therefore, the development of an inexpensive CO₂ reduction-oriented solution is also particularly significant. Exploring SACs containing abundant transition metals that have shown competition capabilities with the rare earth elements is highly recommended. Indeed, non-noble metal catalysts candidates having d electrons and partially occupied orbitals like Fe, Co and Ni have been found to enhance the CO₂ adsorption while promoting desorption of products. They're also less expensive non-noble metals, and cut down on the foreign policy implications of production. Currently, no reported non-noble metal catalyst meets the stringent industrial demands for long-term stability, current densities exceeding 600 mA cm⁻², and FE above 95%. Consequently, the progress of non-noble metal electrocatalysts that can satisfy these industrial requirements is critically needed to advance CO₂-to-CO conversion.
- Upscaling limitations:** The transformation from bench-scale synthesis to industrial-scale production is a serious commercial obstacle due to high equipment cost and the challenge of implementing inefficient production methods under dynamic operating conditions. Thermal pyrolysis and electrochemical synthesis must be explored by the companies to develop SACs in larger batches. The promotion of

Table 5

Comparative evaluation of SAC engineering strategies.

Strategy	Stability	Activity	Synthesis complexity	Scalability	Metal Applicability	Ref
Defect-stabilization	High atom retention (Atomic traps via vacancies, holes, edges, lattice strain)	Moderate reduction (Lower initial ECSA due to site blocking)	Medium (etching, ball-milling and pyrolysis (Annealing synthesis, 500-800 °C)	It shows good scalability	Broad (Fe, Co, Ni, Cu)	[196, 197]
Axial linkage engineering	Medium atomic retention (dynamic but reversible)	High activity (Fe _{CO} via *COOH intermediate stabilization)	Low (impregnation) (one-pot coordination synthesis)	Wide range of scalability due to room-temperature gram-scale	Transition metals like Fe, Ni, Co, Pt, Ir, and Lanthanides	[198, 199]
Heterojunction coordination support	High stability due to electronic anchoring	It shows moderate catalytic activity	High (CVD and ALD)	It has less scalability (lab scale)	Mostly Fe Ni, Co, and Cu	[200]

modern production techniques using automation, motorization, and nano-fabrication explores new pathways for designing SACs.

- c) Fabrication of SAC framework: The in-situ development of the catalyst on the substrate creates a strong and stable bond between them. Axial coordination acts as an additional metal-support binding energy and hinders the metal aggregation. The 3D environment broadens the thermodynamic stability window for single-atom dispersion and facilitates the shortened path for electron transfer, which promotes the overall reaction kinetics. This in-situ method, often guided by a template agent, allows the single atom to be placed precisely and to avoid aggregation.
- d) Strategies to improve the durability: Zn-CO₂ batteries suffer from durability issues because of carbon support corrosion at the high oxidative potential of OER. Consumption of non-carbon templates and developing a higher degree of carbon graphitization are preferred. Furthermore, raising the cathode's OER can improve the battery's energy efficiency by lowering the charging voltage and controlling carbon corrosion.
- e) Highly expensive advanced characterization equipment: Integration of in-situ characterization techniques enables identification of intermediate species, recognition of active sites, and monitoring of SAC dynamics for commercial applications.

6. Summary

Zn-CO₂ batteries offer an attractive approach that integrates renewable energy for converting CO₂ into valuable chemicals during discharge while oxidizing Zn at the anode. It is a CO₂-neutral energy technology with Zn anode offering high specific capacity (~820 mA h g⁻¹, theoretical). Despite these merits, the Zn-CO₂ batteries have faced several challenges in the cathode compartment, such as selectivity towards low-value products, unstable CO₂ reaction kinetics, carbonate formation in aqueous electrolyte, and CO₂ mass transport limitation. On the other hand, the Zn anode counters face issues like dendrites, self-corrosion, and parasitic reactions. Although existing reviews have discussed various CO₂RR catalysts and Zn-CO₂ battery systems, current literature emphasizes either the half-cell CO₂RR or full Zn-CO₂ device broadly without detailed catalytic mechanistic analysis involving SACs. This review highlights the significance of SACs for improving CO₂RR in Zn-CO₂ battery applications. SACs perform a fundamental, superior activity compared to noble and non-noble nanomaterials due to their atomic dispersion of active sites and low metal consumption. The specific axial heteroatom accelerates the kinetics of key intermediates such *COOH, while simultaneously suppressing the HER. Beyond the cathode, SACs function as interfacial regulators for the zinc anode, and they guide zinc nucleation and control water activity at the interface, significantly enhancing long-term stability. This review explores advanced SAC design strategies, including tuning active sites, leveraging effects, axial coordination environment, and exploring non-metal catalyst hybrids, as well as the concept of heteroatom doping.

The electrochemical performance of SAC-incorporated Zn-CO₂ batteries depends on several critical factors, such as ionic conductivity,

electrolyte solvation effect, faradaic efficiency, energy density, and cycle life. To achieve the successful integration of SACs, catalyst design, support materials choice, electrode analyzable structure crafting, and electrolyte adaptation are required. The major obstacle remains the stabilization of single metal atom, which aggregates easily due to high surface energy and low coordination number. Additionally, the lack of proper support materials restricts the number of active sites, and not all metal atoms are easily available to reactants due to uneven distribution. To overcome these challenges, future catalyst development must focus on controlled atomic size and stability of colloidal nanocrystalline particles. Support material with high surface area and rich anchoring sites is important to achieve maximal single-atom loading. Advanced characterization methods and theoretical modelling will be essential for determining the reaction mechanisms and helping the structure-guided design of SACs. Further studies on operando characterization and computations will be crucial for the determination of active sites, stabilization, as well as reaction mechanism. This progress would further facilitate the construction of high-performance SACs for Zn-CO₂ batteries.

CRediT authorship contribution statement

Sowmiya Palaniappan: Writing – original draft, Visualization, Methodology, Investigation, Formal analysis, Data curation. **Jeena Mariya Sebastian:** Writing – original draft, Investigation, Formal analysis, Data curation. **Sakthivel Kaliyaperumal:** Writing – original draft, Investigation, Formal analysis, Data curation. **Padmini Moorthy:** Writing – review & editing, Formal analysis. **Balaji Ramachandran:** Writing – review & editing, Formal analysis. **Narendhar Chandrasekar:** Writing – review & editing, Formal analysis. **Karthik Kiran Sarigamala:** Writing – review & editing, Writing – original draft, Supervision, Project administration, Investigation, Funding acquisition, Formal analysis, Conceptualization.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Data availability

No data was used for the research described in the article.

References

- [1] H. Jafarizadeh, E. Yamini, S.M. Zolfaghari, F. Esmaeilion, M.E.H. Assad, M. Soltani, Navigating challenges in large-scale renewable energy storage: barriers, solutions, and innovations, *Energy Rep.* 12 (2024) 2179–2192.
- [2] Amrouche S. Ould, D. Rekioua, T. Rekioua, S. Bacha, Overview of energy storage in renewable energy systems, *Int. J. Hydrogen Energy* 41 (2016) 20914–20927.
- [3] X.F. Wu, G.Q. Chen, Global primary energy use associated with production, consumption and international trade, *Energy Policy* 111 (2017) 85–94.
- [4] M.A. Hannan, S.B. Wali, P.J. Ker, M.S.A. Rahman, M. Mansor, V. K. Ramachandaramurthy, et al., Battery energy-storage system: a review of technologies, optimization objectives, constraints, approaches, and outstanding issues, *J. Energy Storage* 42 (2021) 103023.
- [5] M. Amir, R.G. Deshmukh, H.M. Khalid, Z. Said, A. Raza, S.M. Mueen, et al., Energy storage technologies: an integrated survey of developments, global economical/environmental effects, optimal scheduling model, and sustainable adaption policies, *J. Energy Storage* 72 (2023) 108694.
- [6] C.J. Fetrov, C. Carugati, X.-D. Zhou, S. Wei, Electrochemistry of metal-CO₂ batteries: opportunities and challenges, *Energy Storage Mater.* 45 (2022) 911–933.
- [7] S. Kaur, M. Kumar, D. Gupta, P.P. Mohanty, T. Das, S. Chakraborty, et al., Efficient CO₂ utilization and sustainable energy conversion via aqueous Zn-CO₂ batteries, *Nano Energy* 109 (2023) 108242.
- [8] L. Tang, H. Peng, J. Kang, H. Chen, M. Zhang, Y. Liu, et al., Zn-based batteries for sustainable energy storage: strategies and mechanisms, *Chem. Soc. Rev.* 53 (2024) 4877–4925.
- [9] X. Zeng, J. Hao, Z. Wang, J. Mao, Z. Guo, Recent progress and perspectives on aqueous Zn-based rechargeable batteries with mild aqueous electrolytes, *Energy Storage Mater.* 20 (2019) 410–437.
- [10] Z.J. Xu, X. Wang, Electrocatalysis: a core technique for a sustainable future, *Chem. Eur. J.* 26 (2020), 3897–3897.
- [11] S.C. Ammal, A. Heyden, Understanding the nature and activity of supported platinum catalysts for the water-gas shift reaction: from metallic nanoclusters to alkali-stabilized single-atom cations, *ACS Catal.* 9 (2019) 7721–7740.
- [12] J. Zhu, G. Zhou, Y. Tong, L. Chen, P. Chen, Vanadium oxide clusters mediated bismuth-tin alloy for accelerated dynamics of electrocatalytic CO₂ conversion, *Adv. Funct. Mater.* 35 (2025) 2420177.
- [13] C. Deng, Z. Wang, L. Feng, S. Wang, J. Yu, Electrocatalysis of sulfur and polysulfides in Li-S batteries, *J. Mater. Chem. A* 8 (2020) 19704–19728.
- [14] X. Liao, R. Lu, L. Xia, Q. Liu, H. Wang, K. Zhao, et al., Density functional theory for electrocatalysis, *Energy Environ. Mater.* 5 (2022) 157–185.
- [15] J. Guo, Y. Haghsheenas, Y. Jiao, P. Kumar, B.I. Yakobson, A. Roy, et al., Rational design of earth-abundant catalysts toward sustainability, *Adv. Mater.* 36 (2024) 2407102.
- [16] MZ Al Mahmud, A concise review of nanoparticles utilized energy storage and conservation, *J. Nanomater.* 2023 (2023) 1–14.
- [17] M. Crespo-Quesada, A. Yarulin, M. Jin, Y. Xia, L. Kiwi-Minsker, Structure sensitivity of alkynol hydrogenation on Shape- and size-controlled palladium nanocrystals: which sites are Most active and selective? *J. Am. Chem. Soc.* 133 (2011) 12787–12794.
- [18] X. Cui, W. Li, P. Ryabchuk, K. Junge, M. Beller, Bridging homogeneous and heterogeneous catalysis by heterogeneous single-metal-site catalysts, *Nat. Catal.* 1 (2018) 385–397.
- [19] H. Wang, Y. Chen, X. Hou, C. Ma, T. Tan, Nitrogen-doped graphenes as efficient electrocatalysts for the selective reduction of carbon dioxide to formate in aqueous solution, *Green Chem.* 18 (2016) 3250–3256.
- [20] H. Zhao, Y. Li, Z. Hu, J. Li, Z. Gong, J. Wang, et al., Toward unlocking the potential of aqueous Zn-CO₂ batteries: what factors affect the electrochemical performance? *Chem. Eng. J.* 510 (2025) 161736.
- [21] Z. Xie, Y. Liu, L. He, J. Chen, X. Wu, M. Li, et al., In situ/operando characterization techniques for reaction interface in electrocatalytic CO₂ reduction, *Small* (2025) 2502083.
- [22] D.S. Su, S. Perathoner, G. Centi, Nanocarbons for the development of advanced catalysts, *Chem. Rev.* 113 (2013) 5782–5816.
- [23] D. Gao, H. Zhou, F. Cai, D. Wang, Y. Hu, B. Jiang, et al., Switchable CO₂ electroreduction via engineering active phases of Pd nanoparticles, *Nano Res.* 10 (2017) 2181–2191.
- [24] X. Wang, J. Xie, M.A. Ghausi, J. Lv, Y. Huang, M. Wu, et al., Rechargeable Zn-CO₂ electrochemical cells mimicking two-step photosynthesis, *Adv. Mater.* 31 (2019) 1807807.
- [25] S. Gao, M. Jin, J. Sun, X. Liu, S. Zhang, H. Li, et al., Coraloid Au enables high-performance Zn-CO₂ battery and self-driven CO production, *J. Mater. Chem. A* 9 (2021) 21024–21031.
- [26] Y. Huang, X. Mao, G. Yuan, D. Zhang, B. Pan, J. Deng, et al., Size-dependent selectivity of electrochemical CO₂ reduction on converted In₂O₃ nanocrystals, *Angew. Chem.* 60 (2021) 15844–15848.
- [27] S. Liu, J. Xiao, X.F. Lu, J. Wang, X. Wang, X.W. Lou, David, Efficient electrochemical reduction of CO₂ to HCOOH over Sub-2 nm SnO₂ quantum wires with exposed grain boundaries, *Angew. Chem. Int. Ed.* 58 (2019) 8499–8503.
- [28] A. Fauzi, X. Chen, H. Zhao, S. Cao, L. Kong, S. Huang, et al., Recent progress of M-N-C single atom electrocatalysts for carbon dioxide reduction reaction, *Energy* 1 (2023) 100045.
- [29] K. Asakura, H. Nagahiro, N. Ichikuni, Y. Iwasawa, Structure and catalytic combustion activity of atomically dispersed Pt species at MgO surface, *Appl. Catal. Gen.* 188 (1999) 313–324.
- [30] M. Flytzani-Stephanopoulos, Q. Fu, H. Saltsburg, Active Nonmetallic Au and Pt Species on Ceria-Based Water-Gas Shift Catalysts, *Science* 301 (2003) 935–938.
- [31] X. Li, X. Yang, J. Zhang, Y. Huang, B. Liu, In situ/operando techniques for characterization of single-atom catalysts, *ACS Catal.* 9 (2019) 2521–2531.
- [32] X. Zhang, H. Shi, B. Xu, Catalysis by gold: isolated surface Au³⁺ ions are active sites for selective hydrogenation of 1,3-Butadiene over Au/ZrO₂ catalysts, *Angew. Chem. Int. Ed.* 44 (2005) 7132–7135.
- [33] B. Qiao, A. Wang, X. Yang, L.F. Allard, Z. Jiang, Y. Cui, et al., Single-atom catalysis of CO oxidation using Pt₁/FeO_x, *Nat. Chem.* 3 (2011) 634–641.
- [34] X. Li, W. Bi, L. Zhang, S. Tao, W. Chu, Q. Zhang, et al., Single-atom Pt as co-catalyst for enhanced photocatalytic H₂ evolution, *Adv. Mater.* 28 (2016) 2427–2431.
- [35] J. Wang, Z. Huang, W. Liu, C. Chang, H. Tang, Z. Li, et al., Design of N-Coordinated dual-metal sites: a stable and active Pt-Free catalyst for acidic oxygen reduction reaction, *J. Am. Chem. Soc.* 139 (2017) 17281–17284.
- [36] N. Daelman, M. Capdevila-cortada, Dynamic charge and oxidation state of Pt/CeO₂ single-atom catalysts, *Nat. Commun.* 18 (2019) 1215–1221.
- [37] S.K. Kaiser, E. Fako, G. Manzocchi, F. Krumeich, R. Hauert, A.H. Clark, et al., Nanostructuring unlocks high performance of platinum single-atom catalysts for stable vinyl chloride production, *Nat. Catal.* 3 (2020) 376–385.
- [38] Z. Qi, Y. Zhou, R. Guan, Y. Fu, J. Baek, Tuning the coordination environment of carbon-based single-atom catalysts via doping with multiple heteroatoms and their applications in electrocatalysis, *Adv. Mater.* 35 (2023) 2210575.
- [39] X. Yue, L. Cheng, C. Guan, Y. Liao, Z. Xu, K.K. Ostrikov, et al., In-plane palladium and interplanar copper dual single-atom catalyst in bulk-like carbon nitride for Cascade CO₂ photoreduction, *Small* 20 (2024) 2308767.
- [40] T. Ren, K. Lu, M. Yin, N. Yan, S. Sai, X. Huang, et al., Single-atom cobalt enables efficient catalytic ozonation for advanced wastewater treatment: mechanisms and application, *Chem. Eng. J.* 500 (2024) 156805.
- [41] S. Jin, Z. Hao, K. Zhang, Z. Yan, J. Chen, Advances and challenges for the electrochemical reduction of CO₂ to CO: from fundamentals to industrialization, *Angew. Chem. Int. Ed.* 60 (2021) 20627–20648.
- [42] Y. Mao, H. Yang, G. Wang, Y. Xu, J. Liu, W. Li, et al., Functional polymers-coated Cu hollow microspheres for CO₂ conversion in primary Zn-CO₂ batteries, *Chem. Eng. J.* 493 (2024) 152856.
- [43] M. Peng, S. Ci, P. Shao, P. Cai, Z. Wen, Cu₃P/C nanocomposites for efficient electrocatalytic CO₂ reduction and Zn-CO₂ battery, *J. Nanosci. Nanotechnol.* 19 (2019) 3232–3236.
- [44] Y. Guo, R. Zhang, S. Zhang, C. Zhi, Recent advances in Zn-CO₂ batteries for the co-production of electricity and carbonaceous fuels, *Nano Mater. Sci.* 7 (2022) 862–876.
- [45] S. Han, D. Ma, Q. Zhu, Atomically structural regulations of carbon-based single-atom catalysts for electrochemical CO₂ reduction, *Small Methods* 5 (2021) 2100102.
- [46] H. Zhao, Y. Zhu, H. Ye, Y. He, H. Li, Y. Sun, et al., Atomic-scale structure dynamics of nanocrystals revealed by in situ and environmental transmission electron microscopy, *Adv. Mater.* 35 (2023) e2206911.
- [47] E.D. Boyes, A.P. LaGrow, M.R. Ward, R.W. Mitchell, P.L. Gai, Single atom dynamics in chemical reactions, *Acc. Chem. Res.* 53 (2020) 390–399.
- [48] S.A. Ali, I. Sadiq, T. Ahmad, Operando characterization technique innovations in single-atom catalyst-derived electrochemical CO₂ conversion, *Chem. Commun.* 61 (2025) 8157–8169.
- [49] S. Nitopi, E. Bertheussen, S.B. Scott, X. Liu, A.K. Engstfeld, S. Horch, et al., Progress and perspectives of electrochemical CO₂ reduction on copper in aqueous electrolyte, *Chem. Rev.* 119 (2019) 7610–7672.
- [50] Y. Liu, J. Chen, W. Li, Y. Zhang, X. Fu, E. Li, et al., Aqueous Zn-CO₂ batteries: a route towards sustainable energy storage, *Ind Chem Mater* 2 (2024) 514–532.
- [51] N. Cheng, L. Zhang, K. Doyle-Davis, S. Sun, Single-atom catalysts: from design to application, *Electrochem. Energy Rev.* 2 (2019) 539–573.
- [52] X. Yang, A. Wang, B. Qiao, J.U.N. Li, Single-atom catalysts: a new frontier in heterogeneous catalysis, *Acc. Chem. Res.* 46 (2013) 1740–1748.
- [53] J. Liu, Catalysis by supported single metal atoms, *ACS Catal.* 7 (2017) 34–59.
- [54] X. Li, X. Yang, Y. Huang, T. Zhang, B. Liu, Supported noble-metal single atoms for heterogeneous catalysis, *Adv. Mater.* 31 (2019) 1902031.
- [55] N. Choudhary, K. Nabeela, N. Mate, S.M. Mobin, Recent advances in CO₂ hydrogenation to methane using single-atom catalysts, *RSC Sustain.* 2 (2024) 1179–1201.
- [56] H.W. Zhu, Y.H. Liu, M.Y. Liu, R.T. Guo, Single-atom catalysts for converting CO₂ into high value-added products: From photocatalysis and electrocatalysis to photoelectrocatalysis, *ChemSusChem* 8 (2025) e202500617.
- [57] X. Guan, C. Zhao, X. Liu, S. Liu, W. Gao, Q. Jiang, Universal principle to describe reactivity and selectivity of CO₂ electroreduction on transition metals and single-atom catalysts, *J. Phys. Chem. C* 124 (2020) 25898–25906.
- [58] L. Zhang, Y. Ren, W. Liu, A. Wang, T. Zhang, Single-atom catalyst: a rising star for green synthesis of fine chemicals, *Natl. Sci. Rev.* 5 (2018) 653–672.
- [59] W. Zhang, Q. Fu, Q. Luo, L. Sheng, J. Yang, Understanding single-atom catalysis in view of theory, *JACS Au* 1 (2021) 2130–2145.
- [60] J. Li, L. Chen, Y. Hao, M. Yuan, J. Lv, A. Dong, et al., Asymmetric coordinated single-atom Pd sites for high performance CO₂ electroreduction and Zn – CO₂ battery, *Chem. Eng. J.* 461 (2023) 141865.
- [61] X. Yao, E. Halpren, Y.Z. Liu, C.H. Shan, Z.W. Chen, L.X. Chen, iScience II intrinsic and external active sites of single-atom catalysts, *iScience* 26 (2023) 107275.
- [62] X. Yu, C. Zhao, Q. Chen, L. Wei, X. Zhao, L. Zhang, et al., First-principles study on the CO₂ reduction reaction (CO₂RR) performance of h-BN-based single-atom catalysts modified with transition metals, *Nanomaterials* 15 (2025) 628.

- [63] S. Back, J. Lim, N.-Y. Kim, Y.-H. Kim, Y. Jung, Single-atom catalysts for CO₂ electroreduction with significant activity and selectivity improvements, *Chem. Sci.* 8 (2017) 1090–1096.
- [64] V. Giullimondi, S. Mitchell, J. Pérez-Ramírez, Challenges and opportunities in engineering the electronic structure of single-atom catalysts, *ACS Catal.* 13 (2023) 2981–2997.
- [65] L. Ling, L. Jiao, X. Liu, Y. Dong, W. Yang, H. Zhang, et al., Potassium-assisted fabrication of intrinsic defects in porous carbons for electrocatalytic CO₂ reduction, *Adv. Mater.* 34 (2022) 2205933.
- [66] Y. Wang, J. Mao, X. Meng, L. Yu, D. Deng, X. Bao, Catalysis with two-dimensional materials confining single atoms: concept, design, and applications, *Chem. Rev.* 119 (2019) 1806–1854.
- [67] N. Cheng, X. Sun, Single-atom catalyst by atomic layer deposition technique, *Chin. J. Catal.* 38 (2017) 150814.
- [68] Y. Chen, Z. Huang, Z. Ma, J. Chen, X. Tang, Fabrication, characterization, and stability of supported single-atom catalysts, *Catal. Sci. Technol.* 7 (2017) 4250–4258.
- [69] Y. Meng, L. Ying, Y. Tao, L. Ma, B. Li, Y. Xing, et al., DFT study on effect of metal type and coordination environment on CO₂ ECR to C1 products over M–N–C catalysts, *ACS Langmuir* 40 (2024) 10663–10675.
- [70] W. Lai, Z. Miao, Y. Wang, J. Wang, S. Chou, Atomic-local environments of single-atom catalysts: synthesis, electronic structure, and activity, *Adv. Energy Mater.* 9 (2019) 1900722.
- [71] T. Zhang, J. Jin, J. Chen, Y. Fang, X. Han, J. Chen, et al., Pinpointing the axial ligand effect on platinum single-atom-catalyst towards efficient alkaline hydrogen evolution reaction, *Nat. Commun.* 13 (2022) 6875.
- [72] M. Yang, S. Li, Y. Wang, J.A. Herron, Y. Xu, L.F. Allard, et al., Catalytically active Au–O(OH)x-species stabilized by alkali ions on zeolites and mesoporous oxides, *Science* 346 (2014) 1498–1501.
- [73] Y. Zhai, D. Pierre, R. Si, W. Deng, P. Ferrin, A.U. Nilekar, et al., Alkali-stabilized Pt–OHx species catalyze low-temperature water-gas shift reactions, *Science* 329 (2010) 1633–1636.
- [74] A. Pedersen, J. Barrio, A. Li, R. Jervis, D.J.L. Brett, M.M. Titirici, et al., Dual-metal atom electrocatalysts: theory, synthesis, characterization, and applications, *Adv. Energy Mater.* 12 (2022) 2102715.
- [75] X. Wang, Q. Zhao, B. Yang, Z. Li, Z. Bo, K.H. Lam, et al., Emerging nanostructured carbon-based non-precious metal electrocatalysts for selective electrochemical CO₂ reduction to CO, *J. Mater. Chem. A* 7 (2019) 25191–25202.
- [76] J. Gu, C.-S. Hsu, L. Bai, H.M. Chen, X. Hu, Atomically dispersed Fe³⁺ sites catalyze efficient CO₂ electroreduction to CO, *Science* 364 (2019) 1091–1094.
- [77] T. Wang, J. Zhang, F. Li, B. Liu, S. Kawi, Recent progress of electrochemical reduction of CO₂ by single atom catalysts, *Mater. Rep. Energy* 2 (2022) 100140.
- [78] S. Li, Z. Kan, H. Wang, J. Bai, Y. Liu, S. Liu, et al., Single-atom photo-catalysts: synthesis, characterization, and applications, *Nano Mater. Sci.* 6 (2024) 284–304.
- [79] C. Gao, J. Low, R. Long, T. Kong, J. Zhu, Y. Xiong, Heterogeneous single-atom photocatalysts: fundamentals and applications, *Chem. Rev.* 120 (2020) 12175–12216.
- [80] Y. Chen, J. Wei, M.S. Duyar, V.V. Ordonsky, A.Y. Khodakov, J. Liu, Carbon-based catalysts for Fischer–Tropsch synthesis, *Chem. Soc. Rev.* 50 (2021) 2337–2366.
- [81] J. Li, C. Chen, L. Xu, Y. Zhang, W. Wei, E. Zhao, et al., Challenges and perspectives of single-atom-based catalysts for electrochemical reactions, *JACS Au* 3 (2023) 736–755.
- [82] Chinese Society of Electrochemistry (CSE), The top ten scientific questions in electrochemistry, *Journal of Electrochemistry* 30 (1) (2024) 2024121.
- [83] W. Li, Z. Guo, J. Yang, Y. Li, X. Sun, H. He, et al., Advanced strategies for stabilizing single-atom catalysts for energy storage and conversion, *Electrochem. Energy Rev.* 5 (2022) 9.
- [84] Liberto G. Di, L. Giordano, G. Pacchioni, Predicting the stability of single-atom catalysts in electrochemical reactions, *ACS Catal.* 14 (2024) 45–55.
- [85] F. Abdelghafar, X. Xu, S. Ping, Z. Shao, Materials reports: energy designing single-atom catalysts toward improved alkaline hydrogen evolution reaction, *Mater. Rep. Energy* 2 (2022) 100144.
- [86] S.J. Tauster, S.C. Fung, R.L. Garten, Strong metal-support interactions. Group 8 noble metals supported on titanium dioxide, *J. Am. Chem. Soc.* 100 (1978) 170–175.
- [87] Y. Zhang, L. Guo, L. Tao, Y. Lu, S. Wang, Defect-based single-atom electrocatalysts, *Small Methods* 3 (2019) 1800406.
- [88] M. Humayun, S. Ali, A. Khan, P. Muhammad Ismail, C. Wang, M. Bououdina, et al., M–N–C single-atom catalysts for electrocatalytic CO₂ reduction: design concept, advanced characterizations, pathways and challenges, *Coord. Chem. Rev.* 538 (2025) 216678.
- [89] T. Tang, L. Ding, Z. Jiang, J. Hu, Advanced transition metal/nitrogen/carbon-based electrocatalysts for fuel cell applications, *Sci. China Chem.* 63 (2020) 1517–1542.
- [90] Y. Li, Z. He, F. Wu, S. Wang, Y. Cheng, S. Jiang, Energy defect engineering of high-loading single-atom catalysts for electrochemical carbon dioxide reduction, *Mater. Rep. Energy* 3 (2023) 100197.
- [91] C. Jia, Q. Sun, R. Liu, G. Mao, T. Maschmeyer, J. Gooding, et al., Challenges and opportunities for single-atom electrocatalysts: from lab-scale research to potential industry-level applications, *Adv. Mater.* 36 (2024) 2404659.
- [92] T. Wei, J. Zhou, X. An, Materials reports: energy recent advances in single-atom catalysts (SACs) for photocatalytic applications, *Mater. Rep. Energy* 4 (2024) 100285.
- [93] X. Wu, H. Zhang, S. Zuo, J. Dong, Y. Li, J. Zhang, Engineering the coordination sphere of isolated active sites to explore the intrinsic activity in single - atom catalysts, *Nano-Micro Lett.* 13 (2021) 136.
- [94] S. Liu, H. Bin Yang, S.F. Hung, J. Ding, W. Cai, L. Liu, et al., Elucidating the electrocatalytic CO₂ reduction reaction over a model single-atom nickel catalyst, *Angew. Chem. Int. Ed.* 59 (2020) 798–803.
- [95] Y. Zhang, L. Jiao, W. Yang, C. Xie, H.L. Jiang, Rational fabrication of low-coordinate single-atom Ni electrocatalysts by MOFs for highly selective CO₂ reduction, *Angew. Chem. Int. Ed.* 60 (2021) 7607–7611.
- [96] W. Zhang, Y. Zhao, W. Huang, T. Huang, B. Wu, Coordination environment manipulation of single atom catalysts: regulation strategies, characterization techniques, and applications, *Coord. Chem. Rev.* 515 (2024) 215952.
- [97] W. Song, C. Xiao, J. Ding, Z. Huang, X. Yang, T. Zhang, et al., Review of carbon support coordination environments for single metal atom electrocatalysts (SACS), *Adv. Mater.* 36 (2024) 2301477.
- [98] X. Wang, Z. Chen, X. Zhao, T. Yao, W. Chen, R. You, et al., Regulation of Coordination Number over Single Co Sites: Triggering the Efficient Electroreduction of CO₂, *Angewandte*, 2018 230029, 1944–1948.
- [99] L. Jiao, H.L. Jiang, Metal-organic-framework-based single-atom catalysts for energy applications, *Chem* 5 (2019) 786–804.
- [100] H. Yang, L. Shang, Q. Zhang, R. Shi, G.I.N. Waterhouse, L. Gu, et al., A universal ligand mediated method for large-scale synthesis of transition metal single atom catalysts, *Nat. Commun.* 10 (2019) 4585.
- [101] C. Zhao, X. Dai, T. Yao, W. Chen, X. Wang, J. Wang, et al., Ionic exchange of metal–organic frameworks to access single nickel sites for efficient electroreduction of CO₂, *J. Am. Chem. Soc.* 139 (2017) 8078–8081.
- [102] Y. Pan, R. Lin, Y. Chen, S. Liu, W. Zhu, X. Cao, et al., Design of single-atom Co–N₂ catalytic site: a robust electrocatalyst for CO₂ reduction with nearly 100% CO selectivity and remarkable stability, *J. Am. Chem. Soc.* 140 (2018) 4218–4221.
- [103] S. Cao, H. Chen, Y. Hu, J. Li, C. Yang, Z. Chen, et al., MXene-based single atom catalysts for efficient CO₂RR towards CO: a novel strategy for high-throughput catalyst design and screening, *Chem. Eng. J.* 461 (2023) 141936.
- [104] Y. Wang, Y. Zhang, W. Yu, F. Chen, T. Ma, H. Huang, Single-atom catalysts for energy conversion, *J. Mater. Chem. A* 11 (2022) 2568–2594.
- [105] X. Zheng, P. Li, S. Dou, W. Sun, H. Pan, D. Wang, et al., Non-carbon-supported single-atom site catalysts for electrocatalysis, *Energy Environ. Sci.* 14 (2021) 2809–2858.
- [106] C. Xie, D. Yan, H. Li, S. Du, W. Chen, Y. Wang, et al., Defect chemistry in heterogeneous catalysis: Recognition, understanding, and utilization, *ACS Catal.* 10 (2020) 11082–11098.
- [107] G. Shi, Y. Xie, L. Du, X. Fu, X. Chen, W. Xie, et al., Constructing Cu–C Bonds in a Graphdiyne-Regulated Cu Single-Atom Electrocatalyst for CO₂ Reduction to CH₄, *Angewandte*, vol. 61, 2022 e202203569.
- [108] Y. Dong, Q. Zhang, Z. Tian, B. Li, W. Yan, S. Wang, et al., Ammonia thermal treatment toward topological defects in porous carbon for enhanced carbon dioxide electroreduction, *Adv. Mater.* 32 (2020) 2001300.
- [109] Y. Zhao, Z. Pei, F. Lu, D. Luan, X. Wang, X. Wen, et al., Rationally designed nitrogen-doped carbon macroporous fibers with loading of single cobalt sites for efficient aqueous Zn–CO₂ batteries, *Chem Catal.* 2 (2022) 1480–1493.
- [110] J. Han, Q. Xu, J. Rong, X. Zhao, P. She, J. Qin, et al., Molecular engineering of porous Fe–N–C catalyst with sulfur incorporation for boosting CO₂ reduction and Zn–CO₂ battery, *Adv. Sci.* 11 (2024) 2407063.
- [111] K. Li, W. Wang, H. Zheng, X. Wang, Z. Xie, L. Ding, et al., Visualizing highly selective electrochemical CO₂ reduction on a molecularly dispersed catalyst, *Mater. Today Phys.* 19 (2021) 100427.
- [112] D. Zhao, K. Yu, P. Song, W. Feng, B. Hu, W.-C. Cheong, Max, et al., Atomic-level engineering Fe₁N₂O₂ interfacial structure derived from oxygen-abundant metal–organic frameworks to promote electrochemical CO₂ reduction, *Energy Environ. Sci.* 15 (2022) 3795–3804.
- [113] S. Liu, L. Wang, H. Yang, S. Gao, Y. Liu, S. Zhang, et al., Nitrogen-doped carbon polyhedrons confined Fe–p nanocrystals as high-efficiency bifunctional catalysts for aqueous Zn – CO₂ batteries, *Small* 18 (2022) 2104965.
- [114] A. Hassan, I. Anis, S. Shafi, A. Assad, A. Rasool, R. Khanam, et al., First-principles investigation of the electrocatalytic reduction of CO₂ on zirconium-based single-, double-, and triple-atom catalysts anchored on a graphitic carbon nitride monolayer, *ACS Appl. Nano Mater.* 5 (2022) 15409–15417.
- [115] X. Zhang, D. Yang, Y. Zhang, W. Zhao, Z. Zhang, Z. Lin, et al., Axial coordination ligands on single-atom catalysts for modulating peroxydisulfate activation pathways to degrade phenoxycarboxylic acid herbicides: a DFT study, *J. Catal.* 457 (2026) 116825.
- [116] L.G.M. Pettersson, A. Nilsson, A molecular perspective on the d-band model: synergy between experiment and theory, *Top. Catal.* 57 (2014) 2–13.
- [117] S.C. Sarma, J. Barrio, A. Bagger, A. Pedersen, M. Gong, H. Luo, et al., Reaching the fundamental limitation in CO₂ reduction to CO with single atom catalysts, *Adv. Funct. Mater.* 33 (2023) 2302468.
- [118] M. Moliner, J.E. Gabay, C.E. Kliever, R.T. Carr, J. Guzman, G.L. Casty, et al., Reversible transformation of Pt nanoparticles into single atoms inside high-silica chabazite zeolite, *J. Am. Chem. Soc.* 138 (2016) 15743–15750.
- [119] T. Zhang, Z. Chen, A.G. Walsh, Y. Li, P. Zhang, Single-atom catalysts supported by crystalline porous materials: views from the inside, *Adv. Mater.* 32 (2020) 2002910.
- [120] S. Yasumura, T. Kato, Y. Qian, T. Toyao, Z. Maeno, K. Shimizu, Dynamic structural evolution of [Rh(NO)₂]⁺ Complex/Rh metal cluster in zeolite during de-NO_x via in situ formed NH₃ under lean/rich periodic conditions, *J. Phys. Chem. C* 126 (2022) 19147–19158.
- [121] H. Zhang, J. Li, S. Xi, Y. Du, X. Hai, J. Wang, et al., A graphene-supported single-atom FeN₃ catalytic site for efficient electrochemical CO₂ reduction, *Angew. Chem. Int. Ed.* 58 (2019) 14871–14876.

- [122] T. Zhang, X. Han, H. Liu, M. Biset-Peiró, J. Li, X. Zhang, et al., Site-specific axial oxygen coordinated FeN₄ active sites for highly selective electroreduction of carbon dioxide, *Adv. Funct. Mater.* 32 (2022) 2111446.
- [123] Z. Chen, A. Huang, K. Yu, T. Cui, Z. Zhuang, S. Liu, et al., Fe₁N₄-O₁ site with axial Fe-O coordination for highly selective CO₂ reduction over a wide potential range, *Energy Environ. Sci.* 14 (2021) 3430–3437.
- [124] J. Huang, X. Qiu, Z. Zhao, H. Zhu, Y. Liu, W. Shi, et al., Single-product faradaic efficiency for electrocatalytic of CO₂ to CO at current density larger than 1.2 cm⁻² in neutral aqueous solution by a single-atom nanozyme, *Angew. Chem.* (2022) 510275, 1–8.
- [125] A. Martini, D. Hursán, J. Timoshenko, M. Rüscher, F. Haase, C. Rettenmaier, et al., Tracking the evolution of single-atom catalysts for the CO₂ electrocatalytic reduction using operando X-ray absorption spectroscopy and machine learning, *J. Am. Chem. Soc.* 145 (2023) 17351–17366.
- [126] J. Song, L. Shi, J. Wei, M. Deng, Z. Qin, L. Yang, et al., Enhancing CO₂ electroreduction over iron-nitrogen-doped carbon catalysts by axial bromine coordination, *Carbon Capture Sci. Technol.* 17 (2025) 100534.
- [127] S. Gong, W. Wang, C. Zhang, M. Zhu, R. Lu, J. Ye, et al., Tuning the metal electronic structure of anchored cobalt phthalocyanine via dual-regulator for efficient CO₂ electroreduction and Zn-CO₂ batteries, *Adv. Funct. Mater.* 32 (2022) 1–14.
- [128] S. Liu, M. Jin, J. Sun, Y. Qin, S. Gao, Y. Chen, et al., Coordination environment engineering to boost electrocatalytic CO₂ reduction performance by introducing boron into single-Fe-atomic catalyst, *Chem. Eng. J.* 437 (2022) 135294.
- [129] W. Zheng, Y. Wang, L. Shuai, X. Wang, F. He, C. Lei, et al., Highly boosted reaction kinetics in carbon dioxide electroreduction by surface-introduced electronegative dopants, *Adv. Funct. Mater.* 31 (2021) 2008146.
- [130] W. Zheng, J. Yang, H. Chen, Y. Hou, Q. Wang, M. Gu, et al., Atomically defined undercoordinated active sites for highly efficient CO₂ electroreduction, *Adv. Funct. Mater.* 30 (2020) 1907658.
- [131] D. Xiang, K. Li, K. Miao, R. Long, Y. Xiong, X. Kang, Amine-functionalized copper catalysts: Hydrogen bonding mediated electrochemical CO₂ reduction to C₂ products and superior rechargeable Zn-CO₂ battery performance, *Acta Phys. Chim. Sin.* 40 (2024) 2308027.
- [132] Z. Zeng, A.G.A. Mohamed, X. Zhang, Y. Wang, Wide potential CO₂-to-CO electroreduction relies on Pyridinic-N/Ni-N_x sites and its Zn-CO₂ battery application, *Energy Technol* 9 (2021) 2100205.
- [133] X. Wang, S. Feng, W. Lu, Y. Zhao, S. Zheng, W. Zheng, et al., A new strategy for accelerating dynamic proton transfer of electrochemical CO₂ reduction at high current densities, *Adv. Funct. Mater.* 31 (2021) 1–9.
- [134] K. Zhao, X. Nie, H. Wang, A. Chen, X. Quan, H. Yu, et al., Selective electroreduction of CO₂ to acetone by single copper atoms anchored on N-doped porous carbon, *Nat. Commun.* 11 (2020) 2455.
- [135] C. Ma, H. Zhang, W. Kong, B. Shen, H. Lyu, Bimetallic atomic Fe-Mn metal-nitrogen active sites for synergistic enhancement of CO₂ electroreduction efficiency, *Environ Funct Mater* 1 (2022) 284–297.
- [136] E. Zhang, T. Wang, K. Yu, J. Liu, W. Chen, A. Li, et al., Bismuth single atoms resulting from transformation of metal-organic frameworks and their use as electrocatalysts for CO₂ reduction, *J. Am. Chem. Soc.* 141 (2019) 16569–16573.
- [137] X. Qin, S. Zhu, F. Xiao, L. Zhang, M. Shao, Active sites on heterogeneous single-iron-atom electrocatalysts in CO reduction reaction, *ACS Energy Lett.* 4 (2019) 1778–1783.
- [138] F. Yang, P. Song, X. Liu, B. Mei, W. Xing, Z. Jiang, et al., Highly efficient CO₂ electroreduction on ZnN₄-based single-atom catalyst, *Angew Chem. Int. Ed. Engl.* 57 (2018) 12303–12307.
- [139] X. Zhang, S. Guo, K.A. Gandionco, A.M. Bond, J. Zhang, Electrocatalytic carbon dioxide reduction : from fundamental principles to catalyst design, *Mater Today Adv* 7 (2020) 100074.
- [140] Y. Zhao, L. Yang, Y. Long, M. Xi, A. Chen, H. Zhang, Efficient optimization of electron transfer pathway by constructing phosphide/ceria interface boosts seawater hydrogen production, *J. Energy Chem.* 95 (2024) 490–498.
- [141] M. Nath, H. Singh, A. Saxena, Direct electrochemistry progress of transition metal chalcogenides as efficient electrocatalysts for energy conversion, *Curr. Opin. Electrochem.* 34 (2022) 100993.
- [142] Z. Zhao, G. Lu, Cu-Based single-atom catalysts boost electroreduction of CO₂ to CH₃OH: first-principles predictions, *J. Phys. Chem. C* 123 (2019) 4380–4387.
- [143] P.-P. Yang, M.-R. Gao, Enrichment of reactants and intermediates for electrocatalytic CO₂ reduction, *Chem. Soc. Rev.* 52 (2023) 4343–4380.
- [144] W. Wu, L. Xu, Q. Lu, J. Sun, Z. Xu, C. Song, et al., Electrocatalysts for acidic CO₂ reduction reaction, *Adv. Mater.* 37 (2025) 2312894.
- [145] G. Marcandalli, M.C.O. Monteiro, A. Goyal, M.T.M. Koper, Electrolyte effects on CO₂ electrochemical reduction to CO, *Acc. Chem. Res.* 55 (2022) 1900–1911.
- [146] H. Zhao, Y. Li, Z. Hu, J. Li, Z. Gong, J. Wang, et al., Toward unlocking the potential of aqueous Zn-CO₂ batteries: what factors affect the electrochemical performance? *Chem. Eng. J.* 510 (2025) 161736.
- [147] B. He, Y. Ge, F. Zhang, H. Tian, Y. Xin, Y. Lei, et al., Understanding electrolytes and interface chemistry for sustainable nonaqueous metal-CO₂ batteries, *Nano-Micro Lett.* 17 (2025) 299.
- [148] J. Liu, J. Yang, Y. Dou, X. Liu, S. Chen, D. Wang, Deactivation mechanism and mitigation strategies of single-atom site electrocatalysts, *Adv. Mater.* 37 (2025) 2420383.
- [149] Y. Cui, C. Ren, M. Wu, Y. Chen, Q. Li, C. Ling, et al., Structure-stability relation of single-atom catalysts under operating conditions of CO₂ reduction, *J. Am. Chem. Soc.* 146 (2024) 29169–29176.
- [150] Y.Q. Su, L. Zhang, Y. Wang, J.X. Liu, V. Muravev, K. Alexopoulos, et al., Stability of heterogeneous single-atom catalysts: a scaling law mapping thermodynamics to kinetics, *Comput Mater* 6 (2020) 144.
- [151] X. Xie, C. He, B. Li, Y. He, D.A. Cullen, E.C. Wegener, et al., Performance enhancement and degradation mechanism identification of a single-atom Co-N-C catalyst for proton exchange membrane fuel cells, *Nat. Catal.* 3 (2020) 1044–1054.
- [152] Z. Chen, F. An, Y. Zhang, Z. Liang, W. Liu, M. Xing, Single-atom Mo-Co catalyst with low biotoxicity for sustainable degradation of high-ionization-potential organic pollutants, *Proc. Natl. Acad. Sci. U. S. A.* 120 (2023) e2305933120.
- [153] Y. Zhang, W. Wan, Y. Peng, Y. Guo, J. Zhou, S. Wang, et al., Corrosion-resistant single-atom catalysts for direct seawater electrolysis, *Natl. Sci. Rev.* 12 (2025) nwaf060.
- [154] A. Kumar, N. Goyal, S. Mathur, A.B. Ibragimov, Y. Zhao, M. Khalid, et al., Advances in coordination engineering of M-N-C single atom catalysts for superior oxygen reduction performance, *Coord. Chem. Rev.* 549 (2026) 217244.
- [155] H. Wang, T. Yang, J. Wang, Z. Zhou, Z. Pei, S. Zhao, Coordination engineering in single-site catalysts: general principles, characterizations, and recent advances, *Chem* 10 (2024) 48–85.
- [156] J. Timoshenko, B. Roldan Cuenya, In situ/operando electrocatalyst characterization by X-ray absorption spectroscopy, *Chem. Rev.* 121 (2021) 882–961.
- [157] A. Martini, J. Timoshenko, M. Rüscher, D. Hursán, M.C.O. Monteiro, E. Liberra, et al., Revealing the structure of the active sites for the electrocatalytic CO₂ reduction to CO over Co single atom catalysts using operando XANES and machine learning, *J. Synchrotron Radiat.* 31 (2024) 741–750.
- [158] Q.-X. Li, D.-H. Si, W. Lin, Y.-B. Wang, H.-J. Zhu, Y.-B. Huang, et al., Highly efficient electroreduction of CO₂ by defect single-atomic Ni-N₃ sites anchored on ordered micro-macroporous carbons, *Sci. China Chem.* 65 (2022) 1584–1593.
- [159] J. Sun, H. Zhou, J. Xu, P. Gao, X. Huang, Y. Li, et al., Self-supporting nickel single atom catalyst derived from nickel metal organic framework for efficient electrocatalysis of CO₂, *J. Alloys Compd.* 1014 (2025) 178780.
- [160] J. Chen, T. Wang, X. Wang, B. Yang, X. Sang, S. Zheng, et al., Promoting electrochemical CO₂ reduction via boosting activation of adsorbed intermediates on iron single-atom catalyst, *Adv. Funct. Mater.* 32 (2022) 2110174.
- [161] T. Wang, X. Sang, W. Zheng, B. Yang, S. Yao, C. Lei, et al., Gas diffusion strategy for inserting atomic iron sites into graphitized carbon supports for unusually high-efficient CO₂ electroreduction and high-performance Zn-CO₂ batteries, *Adv. Mater.* 32 (2020) 2002430.
- [162] T. Zhang, X. Han, H. Liu, M. Biset-Peiró, J. Li, X. Zhang, et al., Site-specific axial oxygen coordinated FeN₄ active sites for highly selective electroreduction of carbon dioxide, *Adv. Funct. Mater.* 32 (2022) 2111446.
- [163] J. Guo, W. Zhang, L.-H. Zhang, D. Chen, J. Zhan, X. Wang, et al., Control over electrochemical CO₂ reduction selectivity by coordination engineering of tin single-atom catalysts, *Adv. Sci.* 8 (2021) 2102884.
- [164] Y. Bao, J. Xiao, Y. Huang, Y. Li, S. Yao, M. Qiu, et al., Regulating spin polarization via axial nitrogen traction at Fe-N₅ sites enhanced electrocatalytic CO₂ reduction for Zn-CO₂ batteries, *Angew. Chem. Int. Ed.* 63 (2024) e202406030.
- [165] S. Chen, J. Chen, Y. Li, S. Tan, X. Liao, T. Zhao, et al., Fe-N₄O-C nanoplates covalently bonding on graphene for efficient CO₂ electroreduction and Zn-CO₂ batteries, *Adv. Funct. Mater.* 33 (2023) 2300801.
- [166] J.-X. Peng, W. Yang, Z. Jia, L. Jiao, H.-L. Jiang, Axial coordination regulation of MOF-Based single-atom Ni catalysts by halogen atoms for enhanced CO₂ electroreduction, *Nano Res.* 15 (2022) 10063–10069.
- [167] D. Gupta, J. Mao, Z. Guo, Bifunctional catalysts for CO₂ reduction and O₂ evolution : a pivotal for aqueous rechargeable Zn-CO₂ batteries, *Adv. Mater.* 36 (2024) 2407099.
- [168] J. Xie, Y. Wang, Recent development of CO₂ electrochemistry from Li-CO₂ batteries to Zn-CO₂ batteries, *Acc. Chem. Res.* 52 (2019) 1721–1729.
- [169] X. Sun, S. Yang, X. Mu, W. Li, C. Sheng, A. Chen, et al., A rechargeable “Rocking Chair” type Zn-CO₂ battery, *Angew. Chem. Int. Ed.* 63 (2024) e202409977.
- [170] H. Liao, H. Xie, S. Zhai, L. Fu, Y. Zhang, S. Hao, et al., A partially Fe-substituted perovskite electrode for enhancing Zn-CO₂ batteries, *Chem. Eng. J.* 474 (2023) 145594.
- [171] S. Yan, C. Peng, C. Yang, Y. Chen, J. Zhang, A. Guan, et al., Electron localization and lattice strain induced by surface lithium doping enable ampere-level electrosynthesis of formate from CO₂, *Angew. Chem.* 60 (2021) 25741–25745.
- [172] Z. Li, J. Jiang, X. Liu, Z. Zhu, J. Wang, Q. He, et al., Coupling atomically dispersed Fe-N₅ sites with defective n-doped carbon boosts CO₂ electroreduction, *Small* 18 (2022) 2203495.
- [173] X. Teng, Y. Niu, S. Gong, M. Xu, X. Liu, L. Ji, et al., In/ZnO@C hollow nanocubes for efficient electrochemical reduction of CO₂ to formate and rechargeable Zn-CO₂ batteries, *Mater. Chem. Front.* 5 (2021) 6618–6627.
- [174] X. Hu, Y. Liu, W. Cui, X. Yang, J. Li, S. Zheng, et al., Boosting industrial-level CO₂ electroreduction of n-doped carbon nanofibers with confined tin-nitrogen active sites via accelerating proton transport kinetics, *Adv. Funct. Mater.* 33 (2023) 2208781.
- [175] W. Yang, Z. Xue, J. Yang, J. Xian, Q. Liu, Y. Fan, et al., Fe nanoparticles embedded in N-doped porous carbon for enhanced electrocatalytic CO₂ reduction and Zn-CO₂ battery, *Chin. J. Catal.* 48 (2023) 185–194.
- [176] J. Chen, Z. Li, X. Wang, X. Sang, S. Zheng, S. Liu, et al., Promoting CO₂ electroreduction kinetics on atomically dispersed monovalent ZnI sites by rationally engineering proton-feeding centers, *Angew. Chem. Int. Ed.* 61 (2022) e20211683.

- [177] J. Wang, Z. Li, Z. Zhu, J. Jiang, Y. Li, J. Chen, et al., Tailoring the interactions of heterostructured $\text{Ni}_4\text{N}/\text{Ni}_3\text{ZnCo}_{0.7}$ for efficient CO_2 electroreduction, *J. Energy Chem.* 75 (2022) 1–7.
- [178] M. Yang, S. Liu, J. Sun, M. Jin, R. Fu, S. Zhang, et al., Highly dispersed Bi clusters for efficient rechargeable $\text{Zn}-\text{CO}_2$ batteries, *Appl. Catal. B Environ.* 307 (2022) 121145.
- [179] R. Yang, J. Xie, Q. Liu, Y. Huang, J. Lv, M.A. Ghausi, et al., A trifunctional Ni-N/P-O-codoped graphene electrocatalyst enables dual-model rechargeable $\text{Zn}-\text{CO}_2/\text{Zn}-\text{O}_2$ batteries, *J. Mater. Chem. A* 7 (2019) 2575–2580.
- [180] Y. Wang, Z. Huang, Y. Lei, J. Wu, Y. Bai, X. Zhao, et al., Bismuth with abundant defects for electrocatalytic CO_2 reduction and $\text{Zn}-\text{CO}_2$ batteries, *Chem. Commun.* 58 (2022) 3621–3624.
- [181] J. Hao, Z. Zhuang, J. Hao, K. Cao, Y. Hu, W. Wu, et al., Strain relaxation in metal alloy catalysts steers the product selectivity of electrocatalytic CO_2 reduction, *ACS Nano* 16 (2022) 3251–3263.
- [182] X. Teng, J. Lu, Y. Niu, S. Gong, M. Xu, T.J. Meyer, et al., Selective CO_2 reduction to formate on a Zn-Based electrocatalyst promoted by tellurium, *Chem. Mater.* 34 (2022) 6036–6047.
- [183] Y. Wang, L. Xu, L. Zhan, P. Yang, S. Tang, M. Liu, et al., Electron accumulation enables Bi efficient CO_2 reduction for formate production to boost clean $\text{Zn}-\text{CO}_2$ batteries, *Nano Energy* 92 (2022) 106780.
- [184] J. Xie, X. Wang, J. Lv, Y. Huang, M. Wu, Y. Wang, et al., Reversible aqueous Zinc- CO_2 batteries based on CO_2 - HCOOH interconversion, *Angew. Chem. Int. Ed. Engl.* 57 (2018) 16996–17001.
- [185] E. Ko, Y.S. Kim, B. Kim, A.R. Mule, C.H. Chung, Efficient CO_2 utilization and sustainable energy conversion via $\text{Zn}-\text{CO}_2$ batteries using gaseous CO_2 , *J. CO₂ Util.* 80 (2024) 102681.
- [186] W. Wang, S. Gong, R. Lu, H. Wang, J. Liu, X. Zhu, et al., In situ growth of Ag aerogels mediating effective electrocatalytic CO_2 reduction and $\text{Zn}-\text{CO}_2$ batteries, *Chem. Eng. Sci.* 280 (2023) 119042.
- [187] S. Gao, S. Chen, Q. Liu, S. Zhang, G. Qi, J. Luo, et al., Bifunctional BiPd alloy particles anchored on carbon matrix for reversible $\text{Zn}-\text{CO}_2$ battery, *ACS Appl. Nano Mater.* 5 (2022) 12387–12394.
- [188] P. Rao, X. Han, H. Sun, F. Wang, Y. Liang, J. Li, et al., Precise synthesis of dual-single-atom electrocatalysts through pre-coordination-directed in situ confinement for CO_2 reduction, *Angewandte* (2025) 202415223.
- [189] X. Sun, Z. Wen, Y. Liu, M. Zhang, W. Li, C. Sheng, et al., A hydrogel electrolyte-based $\text{Zn}-\text{CO}_2$ battery with improved life, *Small* 21 (2025) 2411867.
- [190] J. Wang, M. Zheng, X. Zhao, W. Fan, Structure-performance descriptors and the role of the axial oxygen atom on M-N₄-C single-atom catalysts for electrochemical CO_2 reduction, *ACS Catal.* 12 (2022) 5441–5454.
- [191] B.M. Abraham, O. Piqué, M.A. Khan, F. Viñes, F. Illas, J.K. Singh, Machine learning-driven discovery of key descriptors for CO_2 activation over two-dimensional transition metal carbides and nitrides, *ACS Appl. Mater. Interfaces* 15 (2023) 30117–30126.
- [192] W. Song, C. Xiao, J. Ding, Z. Huang, X. Yang, T. Zhang, et al., Review of carbon support coordination environments for single metal atom electrocatalysts (SACs), *Adv. Mater.* 36 (2024) 2301477.
- [193] L. Zhang, N. Jin, Y. Yang, X.-Y. Miao, H. Wang, J. Luo, et al., Advances on axial coordination design of single-atom catalysts for energy electrocatalysis: a review, *Nano-Micro Lett.* 15 (2023) 228.
- [194] S. Gul, F. Nasim, M.A. Nadeem, Single-atom metal-based electrocatalysts (Fe, Ni, and Co) for CO_2 -to- CO conversion: a comprehensive review, *ACS Appl. Energy Mater.* 8 (2025) 11786–11812.
- [195] C. Chen, J. Li, X. Tan, Y. Zhang, Y. Li, C. He, et al., Harnessing single-atom catalysts for CO_2 electroreduction: a review of recent advances, *EES Catal.* 2 (2024) 71–93.
- [196] Y. Liu, Y. Niu, W. Wang, Y. Hua, Y. Huang, A. Wang, Z. Gao, The role of single-atom catalysts in CO_2 electroreduction: insights into performance, design, and future perspectives, *Sustain. Energy Fuels* (2026). Advance Article.
- [197] D. Zaoralová, R. Langer, M. Otyepka, Iron single-atom catalysts anchored on defect-engineered N-doped graphene reveal an interplay between CO_2 reduction activity and stability, *ACS Sustain. Chem. Eng.* 13 (2025) 8319–8330.
- [198] Y. Gu, H. Chen, J. Shen, Q. Zhang, L. Chen, A first-principles screening for axial ligand regulation of electrocatalytic carbon dioxide reduction on dual-metal atomic catalysts ($\text{M}_1\text{M}_2\text{N}_6\text{-R}$), *ACS Omega* 10 (2025) 37941–37949.
- [199] Z. Bai, X.Z. Jiang, K.H. Luo, Enhanced CO_2 electrochemical reduction on single-atom catalysts with optimized environmental, central and axial chemical ambient, *J. Colloid Interface Sci.* 686 (2025) 1188–1199.
- [200] S. Gong, Y. Zhai, C. Jin, H. Xu, Q. Xia, W. Li, et al., Interface engineering of single-molecular heterojunction catalysts for CO_2 electroreduction in strong acid medium, *Nat. Commun.* 16 (2025) 8704.