

Review

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MOFs-based single/dual-atom catalysts: atomically active sites engineering for efficient CO₂ reduction

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Abstract

The excessive emission of carbon dioxide (CO₂) has seriously threatened the global climate environment and human health; the efficient CO₂ reduction reaction (CO₂RR) as an effective method to reduce CO₂ emissions has become a hot spot in the current catalyst field. Metal-organic frameworks (MOFs) serve as ideal substrates for the preparation of single-atom catalysts (SACs) and dual-atom catalysts (DACs), attributed to their distinctive structure and superior pore characteristics. These catalysts address the issues of inadequate selectivity and activity in CO₂RR by facilitating efficient electron transfer at the atomic level. This review provides an overview of the design strategies for active sites in MOFs-based SACs and DACs, focusing on the synergy between single-atom and multi-atom configurations. It comprehensively summarizes the mechanisms of both photocatalytic and electrocatalytic CO₂RR and the relationship between active sites and catalytic efficiency. Additionally, the review provides an in-depth discussion of their applications in electrocatalysis and photocatalysis of CO₂RR, highlighting specific examples and advancements in these fields. Finally, the challenges of the future directions for active sites design and the development of improving catalytic activity in CO₂RR at industrial current density of MOFs-based SACs/DACs were looked forward.



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Keywords: Metal-organic frameworks, single-atom catalysts, dual-atom catalysts, photocatalysis, electrocatalysis, CO₂RR

INTRODUCTION

In recent decades, the rapid increase of global population has brought about unprecedented energy crises, especially the excessive emission of carbon dioxide (CO₂)^[1-3]. This problem makes the utilization of energy gradually develop towards low-carbon renewable energy^[4-6]. Therefore, the global community is focusing on and advancing the two prominent areas of “carbon peak” and “carbon neutrality” to facilitate the efficient transformation of renewable resources^[7-10]. For this purpose, the development of CO₂ reduction reaction (CO₂RR) has been an effective approach for mitigating CO₂ emissions, thereby addressing the aforementioned environmental challenges^[11-13]. Catalysis is essential for enhancing both electrocatalytic and photocatalytic efficiency in CO₂RR^[14-16]. The development of high-efficiency catalysts represents a significant global challenge, because the utilization of highly efficient catalysts can effectively expedite the kinetics of chemical reactions^[17-19]. The catalytic activity is determined by the number of active sites present on the catalyst^[20-22]. Numerous studies have demonstrated that the atomic utilization efficiency of metal active sites is exceptionally high, which can be close to 100%, encouraging increased catalyst research to focus on the dispersion system with atomic level^[23-26].

Single/dual-atom catalysts (SACs/DACs), with atomic-scale catalytic active sites, are the most emerging catalyst material in the field of efficient CO₂RR^[27-29]. The most typical advantages of SACs/DACs are that they have clear coordination structure, optimal atomic utilization and distinctive electronic configuration, which are crucial for the precise regulation of active catalytic sites^[30-33]. However, when dispersed to the atomic scale, the high surface energy of metal atoms prevents them from achieving good dispersion and thus clumping together, greatly reducing the catalytic efficiency of SACs/DACs^[34-37]. Previous research has demonstrated that the synthesized atomic-scale SACs/DACs exhibit low structural porosity and limited metal loading capacity^[38-40]. Therefore, it is particularly critical to find suitable porous carrier materials to provide stable and effective support for metal atoms of SACs/DACs^[41-43]. Among them, metal-organic frameworks (MOFs) are very suitable porous carrier materials for SACs/DACs^[44,45].

MOFs are a kind of porous crystal framework that is formed by the combination of metal active center (ion or cluster) and organic macromolecule (N-containing or carboxylic acid ligands) through strong coordination^[46-48]. The advantages of MOFs are also obvious, such as the controllable composition of metal and organic connections, large specific surface area, both metal-organic composite properties, controllable porous structure and precise active adsorption sites^[49-51]. Coupled with high porosity and high metal loading rate, pristine MOFs are already one of the best carrier choices for atomic-level catalysts^[52-54]. In addition, derivatives (porous carbon/metal matrix) obtained by carbonization, calcination and other pyrolysis treatments of MOFs have been widely used as carriers for fixing precisely active catalytic sites at the atomic dispersion scale^[55-58]. With distinctive structure and superior pore characteristics, MOFs serve as ideal substrates for the preparation of SACs and DACs (MOFs-based SACs/DACs)^[59-61].

So far, the MOFs-based SACs/DACs have shown a strong performance advantage in efficient electrocatalytic and photocatalytic of CO₂RR and address the issues of inadequate selectivity and activity in CO₂RR by facilitating efficient electron transfer at the atomic level^[62-64]. The studies of the design strategies for active sites in MOFs-based SACs and DACs were systematically summarized herein in this review, focusing on the synergy between single-atom and multi-atom configurations. The review comprehensively summarizes the mechanisms of both photocatalytic and electrocatalytic CO₂RR (ECRR) and the relationship between active sites and catalytic efficiency. Additionally, the review provides an in-depth discussion of their applications in photocatalysis and electrocatalysis of CO₂RR, highlighting specific

examples and advancements in these fields [Figure 1]. Finally, the prospects of the future directions of MOFs-based SACs/DACs in CO₂RR were looked forward to further improving the catalytic activity at industrial current density.

DESIGN STRATEGIES FOR ACTIVE SITES: FROM SINGLE-ATOM TO MULTI-ATOMS COORDINATION

For the catalyst, the most concerned performance is the level of catalytic activity^[65-67]. In order to obtain MOFs-based SACs/DACs with high catalytic activity, the design strategies for active sites are of critical importance, as well as the characterization of active sites^[68-70]. In this part, we systematically concluded the design and regulation of MOFs-based SACs/DACs active sites together with the characterization of active sites.

Design and regulation of MOFs-based SACs active sites

MOFs-based SACs literally stand for SACs obtained from MOFs, for example, original MOFs and materials derived from MOFs (carbonaceous material, metal oxides, or other substances)^[71,72]. Unlike single-site heterogeneous catalysts, the active sites in MOFs-based SACs are formed by completely isolated metal atoms that do not interact with each other^[46,73,74]. Therefore, the design and regulation of active sites directly affect the catalytic efficiency of MOFs-based SACs^[75-77].

The single atomic active sites in MOFs-based SACs could be roughly categorized into three distinct types according to the location or connection mode of the active sites in MOFs [Figure 2]: (1) MOFs skeleton limited single-atom sites. With the three-dimensional frame structure, MOFs could incorporate metal-based substances to create final single-atom metal active sites by hosting a variety of functional guest substances within their pores^[78-81]; (2) ligands regulated single-atom sites. The organic ligands in MOFs contain abundant chelating binding sites, providing sufficient binding locations for single metal atoms sites^[82-85]; (3) defect engineering regulated single-atom sites. Defects in MOFs (mainly referred to as metal nodes), with higher energy state, could be fully combined with heterogeneous metal atoms to form single-atom active sites^[86-90]. In this part, synthesis strategies and works of MOFs-based SACs would be discussed around spatial skeleton, ligand regulation and defect regulation of single-atom sites.

MOFs skeleton limited single-atom sites

Isolating metal atoms within the rigid structure of MOFs effectively restricts the mobility of single atoms, preventing their aggregation and ensuring their stability during catalytic processes^[91-93]. The MOFs structure provides a tunable environment that could optimize the electronic features and coordination states of the single atomic sites^[94-96]. This spatial confinement enhances the mutual influence of the active sites on reactants, thereby improving activation efficiency^[97-99]. By leveraging the unique characteristics of MOFs, such as tunable porosity and functionalization, skeleton-limited single-atom sites are applicable to a variety of chemical reactions^[100-102].

Zuo *et al.* prepared Co SACs supported on ultrathin MOFs nanosheets (Co-MNSs) according to a bottom-up synthetic strategy [Figure 3A]^[103]. Co single atoms were fixed on the ultra-thin MOFs nanosheets and Co-N₄ moiety functioned as active sites. By lowering the energy barrier and enhancing charge separation, the ultrathin structure increased accessible sites and facilitated CO₂ adsorption to form reactive radicals, thereby improving photocatalytic CO₂RR. Xie *et al.* prepared a series of M-N-C-based SACs using a direct pyrolysis method [Figure 3B]^[104]. The strong coordination bonds between metal and nitrogen effectively anchored the metal single atoms onto the nitrogen-doped carbon support obtained from ZIF-8. In the process of synthesizing M-N-C-based SACs, the porous structure of ZIF-8 effectively restricted the

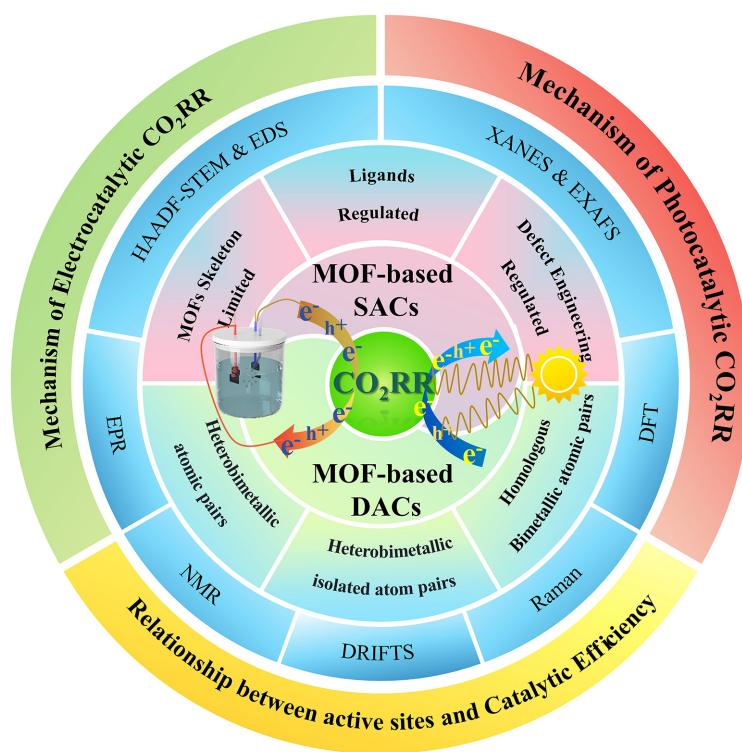


Figure 1. Overview of MOFs-based SACs/DACs for efficient CO₂RR: design and characterization of active sites and mechanism analysis. MOF: Metal-organic framework; SACs: single-atom catalysts; DACs: dual-atom catalysts; CO₂RR: CO₂ reduction reaction; HAADF-STEM: high-angle annular dark field scanning transmission electron; EDS: energy-dispersive X-ray spectroscopy; XANES: X-ray absorption near-edge structure; EXAFS: extended XAFS; DFT: density functional theory; DRIFT: diffuse reflectance infrared fourier transform; NMR: nuclear magnetic resonance; EPR: electron paramagnetic resonance.

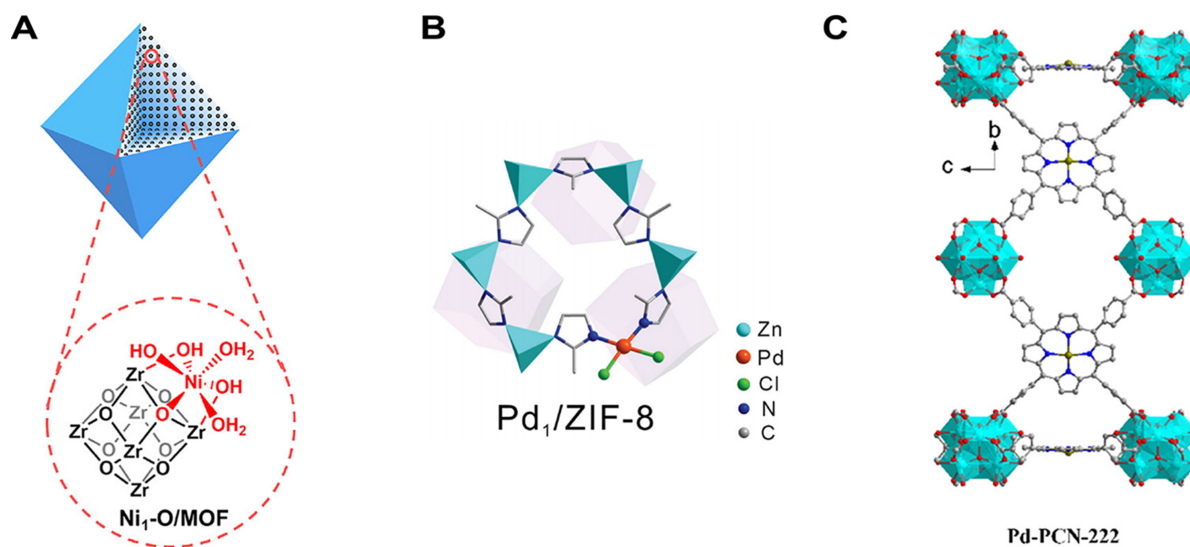


Figure 2. (A) Structure diagram of MOFs skeleton limited single-atom sites, quoted with permission from Leng et al.^[81]; (B) Structure diagram of Ligands regulated single-atom sites, quoted with permission from Chen et al.^[85]; (C) Structure diagram of defect engineering regulated single-atom sites, quoted with permission from Zhang et al.^[90]. MOFs: Metal-organic frameworks; ZIF: zeolitic imidazolate framework; PCN: porous coordination network.

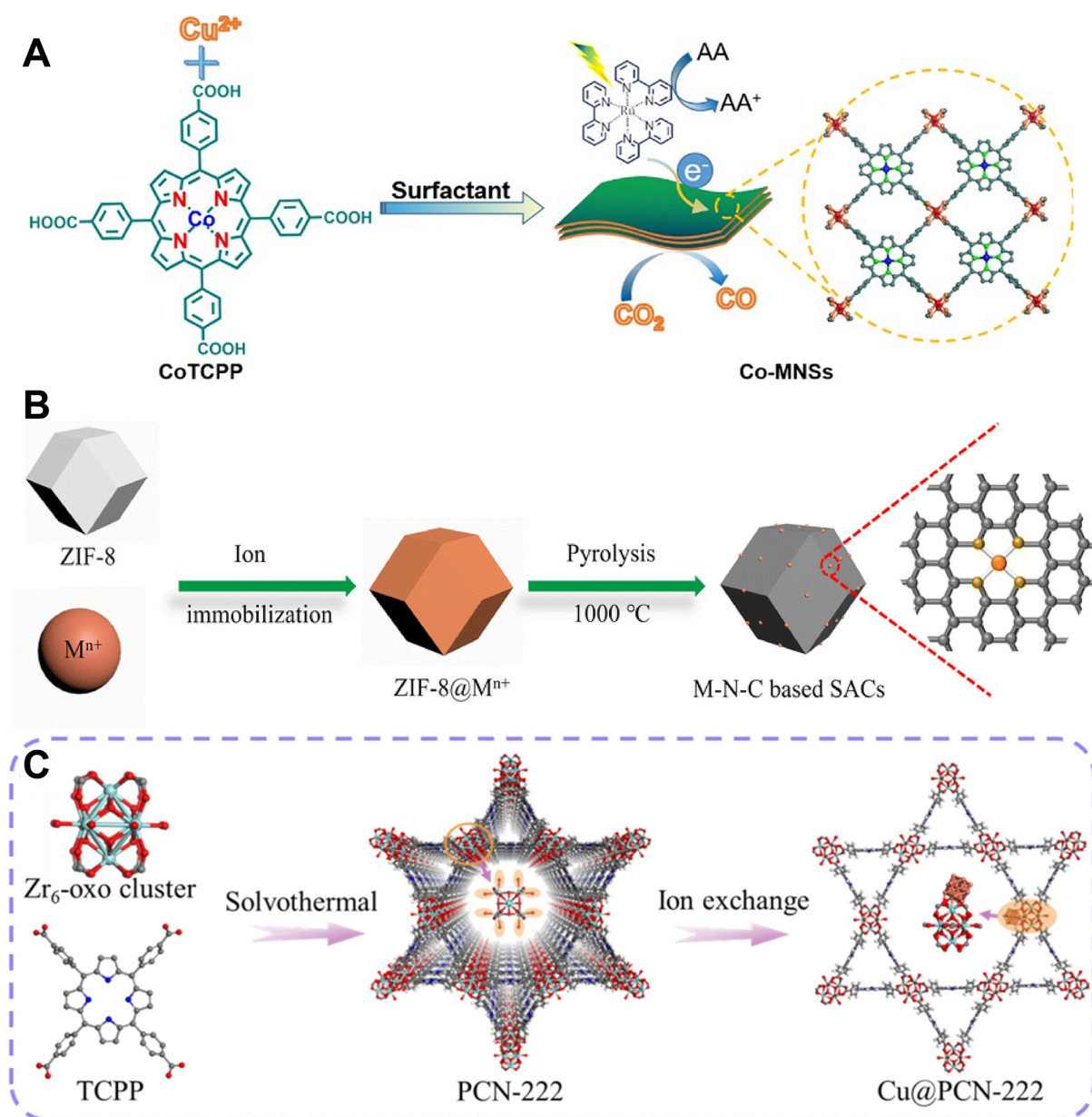


Figure 3. (A) Schematic diagram of fabrication of Co-MNSs for photocatalytic CO₂RR, quoted with permission from Zuo *et al.*^[103]; (B) Schematic diagram of preparation of M-N-C based SACs for electrocatalytic CO₂RR, quoted with permission from Xie *et al.*^[104]; (C) Schematic diagram of fabrication of Cu/PCN-222, quoted with permission from Bao *et al.*^[105]. ZIF: Zeolitic imidazolate framework; SACs: single-atom catalysts; TCPP: tetrakis(carboxyphenyl)phthalocyanine cobalt; MNSs: metal-nitrogen supramolecular structure.

dispersion of metal single atoms, preventing their agglomeration. Additionally, through the ion exchange strategy, the abundant terminal -OH groups on the Zr₆(μ₃-OH)₈(OH)₈(CO₂)₈ clusters in PCN-222 were deprotonated and utilized to anchor Cu on the Zr₆-oxo nodes and stabilizing Cu in the nanopores of PCN-222 by Bao *et al.* [Figure 3C]^[105]. This pore confinement effect enabled Cu and Zr₆-oxo clusters to join closely via the Zr⁴⁺-O²⁻(-Cu²⁺) and Zr⁴⁺-Cu²⁺ interface sites, which also led to the alteration of the electronic structure of Cu.

Ligands regulated single-atom sites

By coordinating with isolated metal atoms, ligands could adjust the associated electronic characteristics and coordination settings, influencing the catalytic efficacy^[106-108]. The choice of ligands affects the oxidation condition, electron spreading, and steric hindrance around the metal centers, which could enhance reactivity and selectivity in catalytic processes^[109-111]. Additionally, ligands could stabilize single-atom sites, prevent aggregation and ensure their availability for reactions^[112-114]. This ligand regulation mechanism allows for the precise tuning of catalytic performance, making it a vital strategy in the programming of effective single atomic catalysts for various chemical applications^[115-117].

Chen *et al.* designed a MOF (UiO-67) encapsulated N-heterocyclic carbene (NHC) linked copper single atom site (Cu SAS) catalyst (2Bn-Cu@UiO-67) using a multi-step method [Figure 4A]^[118]. The catalyst's porosity promoted CO₂ diffusion to 2Bn-Cu sites. The NHC ligand was crucial in determining the catalyst's property, influencing the electronic structure and interactions of Cu SAS with reactants, and enhancing CO₂ RR activity. To optimize catalytic performance for single atoms, modifying ligands to regulate the coordination condition around the catalytic sites was essential. Wang *et al.* developed a series of single cobalt (Co) site catalysts, UiO-Co-N_x (x = 2, 3, 4), using a mixed ligand and post-synthetic modification strategy [Figure 4B]^[119]. This was achieved by reacting hexahydrated cobalt chloride with ligands such as 2-phenylpyridine and 2,2'-bipyridine at presence of UiO-67-20% bipyridine, thereby anchoring the single Co sites within the UiO-type MOF. The underlying mechanism revealed that varying the nitrogen coordination number influenced the electronic density and charge transfer kinetics of the Co sites. Notably, UiO-Co-N₃ exhibited optimal performance, demonstrating the fastest charge transfer rate and the minimum energy obstacles for both the rate-determining procedure in CO₂ reduction and CO desorption. Additionally, Dong *et al.* utilized the Ni-MOF-74 synthesis approach to fabricate a mesoporous Ni-74-Am [Figure 4C]^[120]. Ni-74-Am, an amorphous MOF with ligand defects, had more unsaturated Ni active sites, enhancing photocatalytic CO₂ reduction. Under visible light, it achieved a 1.38 mmol·g⁻¹·h⁻¹ CO generation rate and 94% CO selectivity, due to its suitable valence and band structure, high electron-hole separation efficiency, and fast carrier migration rate.

Defect engineering regulated single-atom sites

Introducing defects such as vacancies or interstitials could alter the local environment around metal centers, thereby affecting their electronic structure and reactivity^[121-123]. These defects could create additional active sites and contribute to the stabilization of isolated metal atoms, preventing their aggregation^[124-126]. Furthermore, they could modify the adsorption characteristics of reactants, facilitating more efficient catalytic pathways^[122,127,128]. This strategic manipulation of defects allows for the fine-tuning of single atomic catalysts, enhancing their performance for various catalytic processes^[129-131].

Huang *et al.* synthesized a core-shell structured heterojunction catalyst based on Co and Zn atoms (Co₃S₄/NC@ZnS/NC) using a MOFs-on-MOFs strategy [Figure 5A]^[132]. Analysis confirmed a higher sulfur-vacancy concentration in Co₃S₄/NC@ZnS/NC than in Co₃S₄/NC. The interaction between ZIF-67 and ZIF-8, along with subsequent transformations, located the Co and Zn atoms at specific locations within the core-shell structure. This arrangement, along with the carbon-nitrogen-doped matrix and the formation of sulfides, maintained a relatively stable distribution, enabling effective immobilization. Shan *et al.* synthesized UiO-66-based Cu SACs via solvothermal method. Defect engineering retained the MOF framework integrity [Figure 5B], with Cu²⁺ anchored at UiO-66 defect sites (-OH/-OH₂) to form Cu-O coordination structures [Figure 5C]. Energy-dispersive X-ray spectroscopy (EDS) elemental mapping confirmed uniform Cu distribution across the support [Figure 5D]^[133]. Additionally, Wen *et al.* developed a microwave-assisted rapid pyrolysis approach for the preparation of carbon-based SACs (Ni₁NC), in which Ni was implanted in

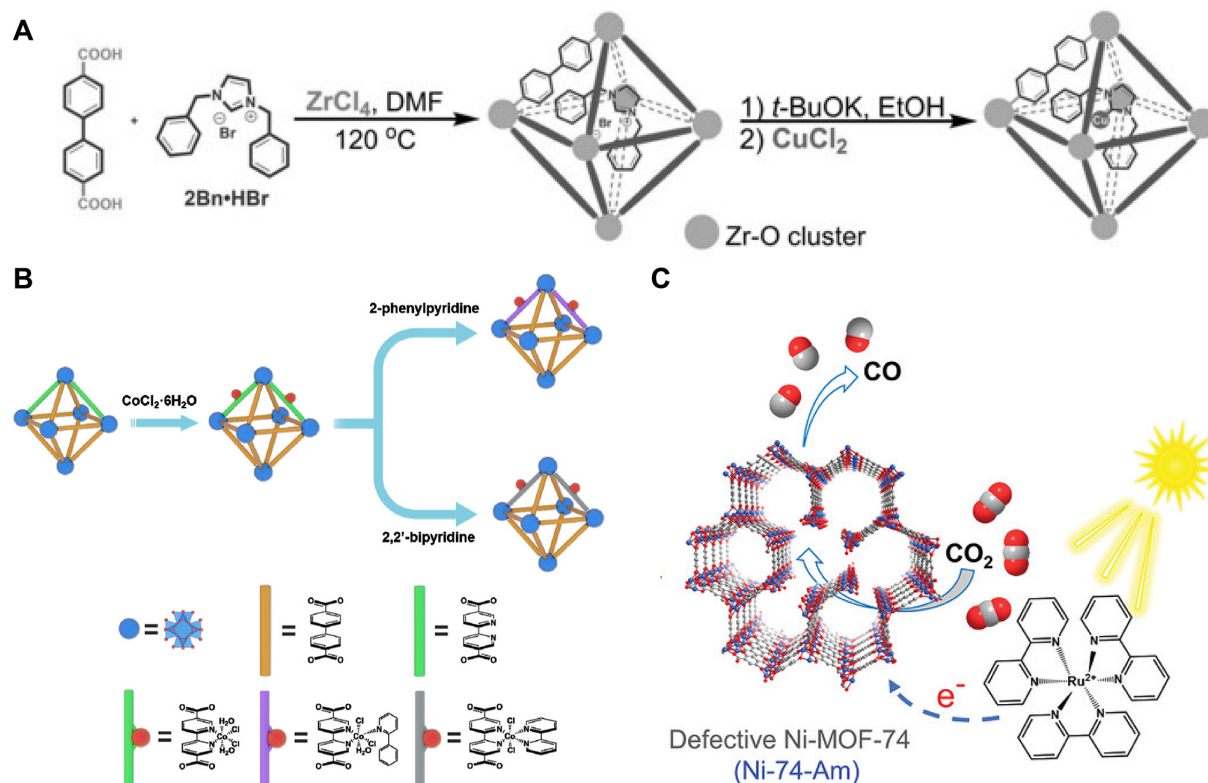


Figure 4. (A) Schematic diagram of fabrication of 2Bn-Cu@UiO-67, quoted with permission from Chen *et al.*^[118]; (B) Preparation strategy of UiO-Co-N_x (x = 2, 3, 4), quoted with permission from Wang *et al.*^[119]; (C) Schematic diagram of fabrication of Ni-74-Am, quoted with permission from Dong *et al.*^[120]. DMF: N,N-dimethylformamide; MOF: metal-organic framework.

N-doped carbon [Figure 5E]^[134]. The aberration-corrected high-angle annular dark field scanning transmission electron microscopy (HAADF-STEM) results obviously demonstrated that Ni was dispersed in a single atomic state [Figure 5F].

Design and synergistic effects of MOFs-based DACs active sites

Owing to the synergistic effect between the dual-atomic active sites, it has been demonstrated that the catalytic performance of MOFs-based DACs markedly outperforms that of MOFs-based SACs. MOFs-based DACs referred to the direct or indirect establishment of DACs with MOFs as the basic materials^[135-137]. With the support of proper preparation methods and frame structure, the bimetallic atoms are uniformly dispersed in the MOFs^[138-140]. The derivatives of the MOFs precursors obtained by pyrolysis such as carbonization or calcination could be loaded with various dual-atom metal catalytic sites^[141-143]. In MOFs-based DACs, adjacent metal atoms are directly or indirectly linked together to form two catalytic sites. These metal atoms could be homologous or heterologous, usually connected with some non-metallic atoms featuring high electronegativity, including elements such as N, S, O, or C^[144-146]. According to the type of metal atoms at the catalytic sites and the connection mode, MOFs-based DACs were usually divided into three types: homologous bimetallic atomic pairs, heterobimetallic isolated atom pairs and heterobimetallic atomic pairs [Figure 6]^[147-149]. Each of these types would be discussed in detail in different sections below.

Homologous bimetallic atomic pairs

For homologous bimetallic atomic pairs, the active catalytic sites are formed by the cooperative interaction between the same metallic atoms with the non-metallic chelating elements (such as N) [Figure 6A]^[152-154].

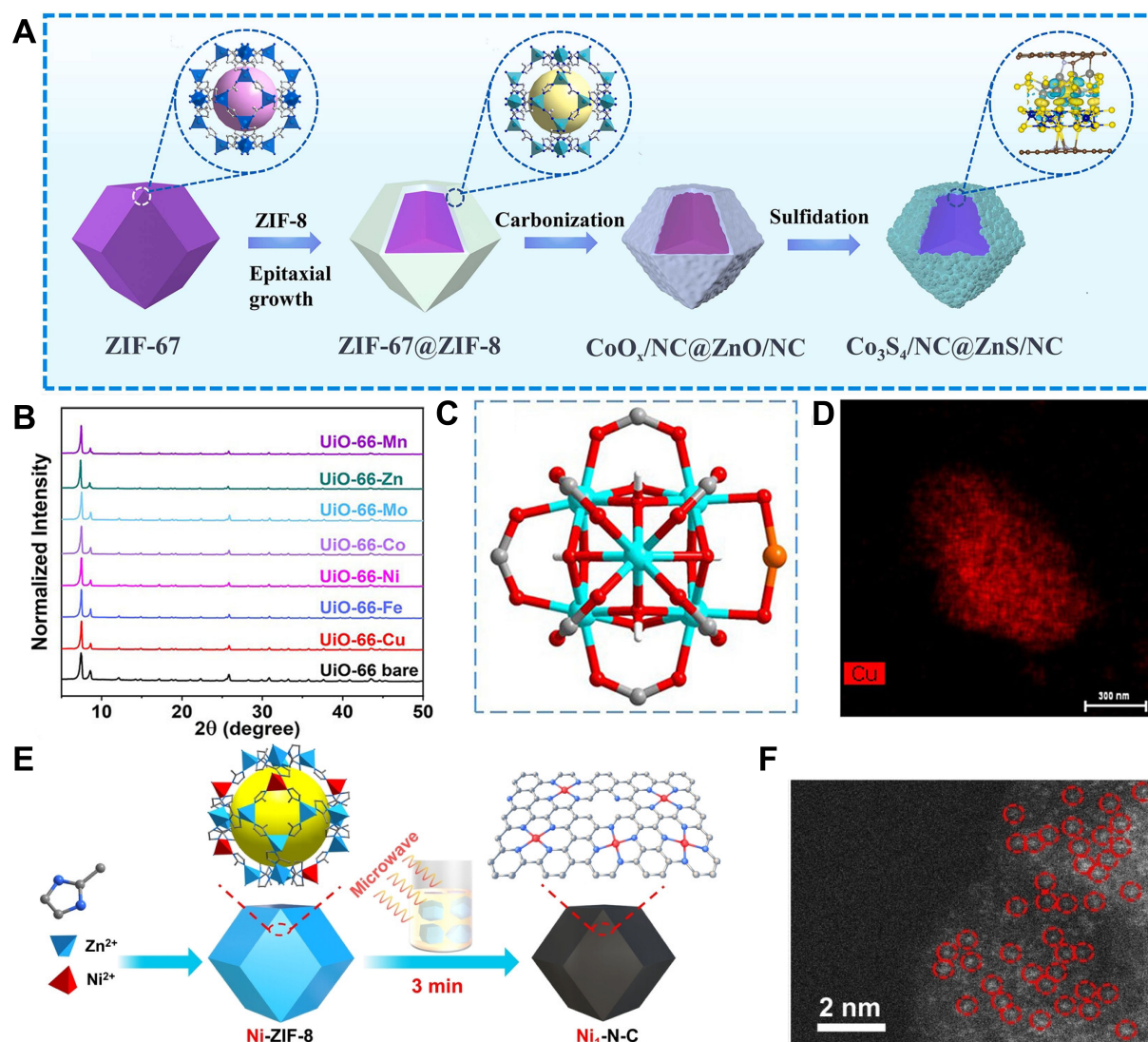


Figure 5. (A) Schematic diagram of fabrication of $\text{Co}_3\text{S}_4/\text{NC}@\text{ZnS}/\text{NC}$, quoted with permission from Huang *et al.* [132]; (B) PXRD patterns of bare UiO-66-defect and UiO-66-M materials; (C) View of the structure of the cluster node in UiO-66-Cu incorporating a single Cu(II) center at the defect site. Color scheme: Cu, orange; O, red; C, grey; H, white; (D) The EDS elemental mapping images of UiO-66-Cu; (B-D) are quoted with permission from Shan *et al.* [133]; (E) Preparation strategy of Ni_1NC ; (F) Aberration-corrected HAADF-STEM image of Ni_1NC ; (E and F) are quoted with permission from Wen *et al.* [134]. ZIF: Zeolitic imidazolate framework; PXRD: powder X-ray diffraction; EDS: energy-dispersive X-ray spectroscopy; HAADF-STEM: high-angle annular dark field scanning transmission electron microscopy.

CO_2RR requires high selectivity and stability of catalyst, which brings difficulty to the design and application of MOFs-based DACs with homologous bimetallic atomic pairs [155–157].

Based on a two-step template-assisted method, Wang *et al.* prepared precursor Fe-ZIF-8 by a host-guest encapsulation strategy. Then, through 950°C pyrolysis under a 95% Ar + 5% H_2 mixed atmosphere for one hour, a dual-atom iron sites electrocatalyst with N-doped carbon matrix ($\text{Fe}_2\text{-N}_6\text{-C}$ DAC) was obtained [Figure 7A] [158]. At the same time, to have a reference object, a single-atom electrocatalyst ($\text{Fe}_1\text{-N}_4\text{-C}$ SAC) was prepared by using a similar route under pure Ar gas. Results of X-ray diffraction (XRD) pattern showed that $\text{Fe}_2\text{-N}_6\text{-C}$ DAC and $\text{Fe}_1\text{-N}_4\text{-C}$ SAC both had two wide diffraction peaks at the same position, indicating that they both belonged to the graphitic carbon structure [Figure 7B]. By detecting the linear sweep

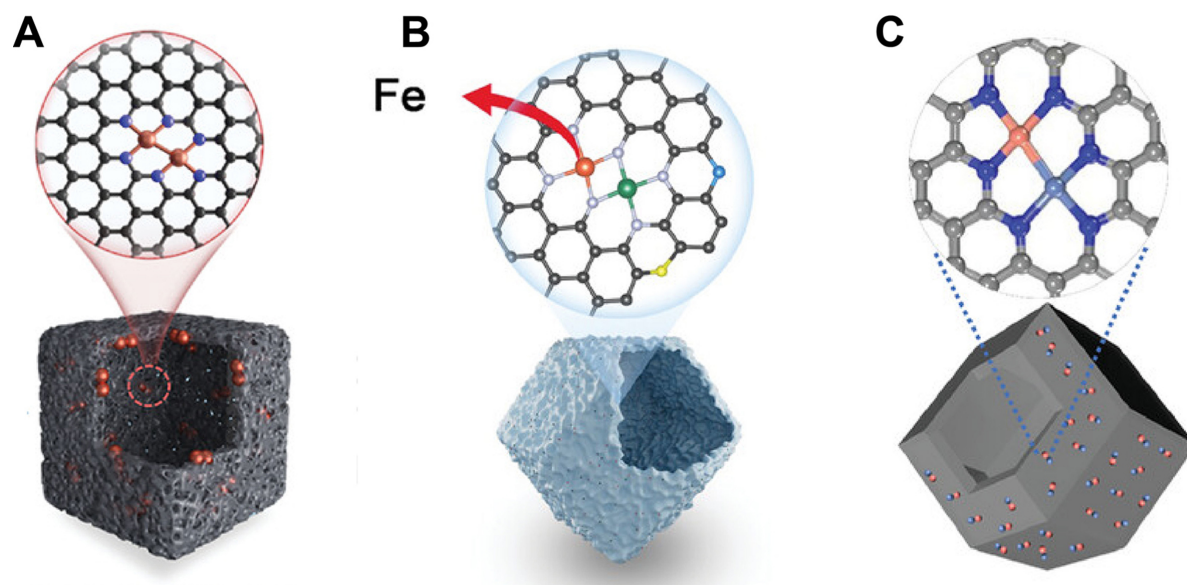


Figure 6. (A) Structure diagram of homologous bimetallic atomic pairs, quoted with permission from Leng *et al.*^[150]; (B) Structure diagram of heterobimetallic isolated atom pairs, quoted with permission from Chen *et al.*^[135]; (C) Structure diagram of heterobimetallic atomic pairs, quoted with permission from Zhang *et al.*^[151].

voltammetry (LSV) curves and Faradaic efficiency for CO (FE_{CO}) of different Fe_x-N_y-C catalysts, Fe_2-N_6-C DAC showed a much better CO_2RR catalytic activity, with FE_{CO} 80% higher than that of Fe_1-N_4-C SAC [Figure 7C and D]. Coincidentally, Zhao *et al.* did a similar job, with the same metal, precursor, and preparation method. The only difference was that the pyrolysis of Fe-ZIF-8 precursor was carbonized for three h under 1,000 °C nitrogen atmosphere, and then the DAC with nitrogen-doped porous carbon anchored (Fe_2NPC) was obtained [Figure 7E]^[159]. With only 60 $mV \cdot dec^{-1}$ Tafel slope, the FE_{CO} of Fe_2NPC could reach 96% at -0.6 V (RHE), showing superior CO_2RR electrocatalytic activity [Figure 7F and G].

Heterobimetallic isolated atom pairs

Contrary to homologous bimetallic atomic pairs, the active sites in the catalytic center assembled with the coordination of heterogeneous metallic atoms with N atoms are called heterobimetallic isolated atom pairs [Figure 6B]^[160–162]. Jiao *et al.* collected dual-atom Fe and Ni incorporated into N-Doped carbonaceous material derived from MOFs by a Zn-assisted atomization strategy [Figure 8A]^[163]. First, Fe-ZnO and Ni-ZnO were prepared by solvothermal method. Then, under the self-assembly action of homogeneous mixing, Fe-ZnO and Ni-ZnO were combined with ZIF-8 through electrostatic interaction, forming Fe&Ni-ZnO/ZIF-8 DACs MOFs-based composite material. Finally, a ZIF-8 derived DAC with adjacent Fe- N_4 and Ni- N_4 isolated pairs (named Fe_1-Ni_1-N-C) was obtained after pyrolytic reaction of Fe&Ni-ZnO/ZIF-8 composite. Fe_1-Ni_1-N-C exhibited a hollow and porous architecture, significantly enhancing mass transport and facilitating rapid access for efficient electron transfer between the catalytic sites and the reactants. Additionally, the synergistic interaction between Fe- N_4 and Ni- N_4 catalytic centers was vital in boosting catalytic activity through the optimization of their electronic configurations. Surprisingly, compared to other reference catalysts, Fe_1-Ni_1-N-C showed excellent performance for ECRR with FE_{CO} of 96.2% at -0.5 V [Figure 8B and C].

Heterobimetallic atomic pairs

For heterobimetallic atomic pairs, the active catalytic sites are formed by direct connections between different dual-metal atoms in addition to coordination connections by metal and N atoms, *etc.*

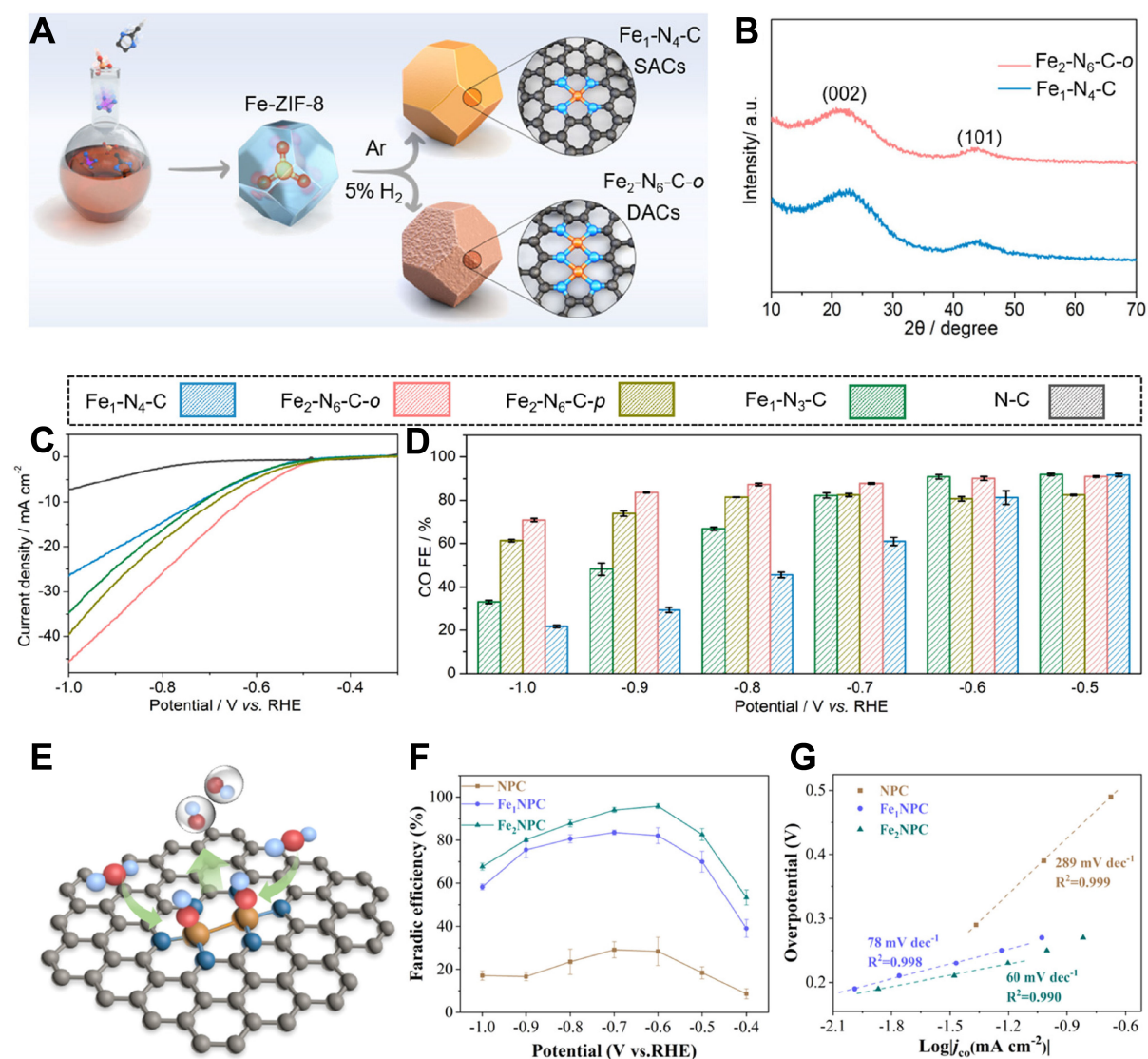


Figure 7. (A and B) Schematic diagram of fabrication (A) and XRD spectrum (B) of Fe₁-N₄-C SAC and Fe₂-N₆-C DAC; (C and D) LSV curves (C) and FE_{CO} test (D) of different Fe_x-N_y-C catalysts; (A-D) are quoted with permission from Wang *et al.* [158]; (E) Structure diagram of Fe₂NPC; (F and G) FE_{CO} (F) and J_{CO} (G) of Fe₂NPC and other reference catalysts; (E-G) are quoted with permission from Zhao *et al.* [159]. SACs: Single-atom catalysts; DACs: dual-atom catalysts; RHE: reversible hydrogen electrode; XRD: X-ray diffraction; LSV: linear sweep voltammetry; FE_{CO}: Faradaic efficiency for CO.

[Figure 6C] [164-166]. Therefore, there has been a stronger synergistic effect between the heterobimetallic atomic active sites than homologous bimetallic atomic pairs or heterobimetallic isolated atom pairs [167-169]. Zhang *et al.* designed a NiN₃@CoN₃ sites loaded on nitrogen-doped graphitized carbon catalysts (NiN₃@CoN₃-NC) [Figure 8D] [170]. Zn/Co-ZIFs as precursor was prepared by classical solvothermal method with cobalt salt, zinc salt and 2-methylimidazole in methanol. Then Zn/Co/Ni-ZIFs was obtained by mixing nickel salt and Zn/Co-ZIFs through ion exchange and adsorption. The final product NiN₃@CoN₃-NC was obtained by pyrolysis and pickling (H₂SO₄) of Zn/Co/Ni-ZIFs. The high-resolution transmission electron microscopy (HRTEM) image revealed that NiN₃@CoN₃-NC featured a graphite and disordered carbon biphasic structure, with no detection of Ni or Co nanoparticles [Figure 8E]. The HAADF-STEM elemental mapping images demonstrated that NiN₃@CoN₃-NC exhibited a homogeneous distribution of C, N, Ni, and Co, particularly highlighting an atomic-level dispersion of Ni and Co [Figure 8F].

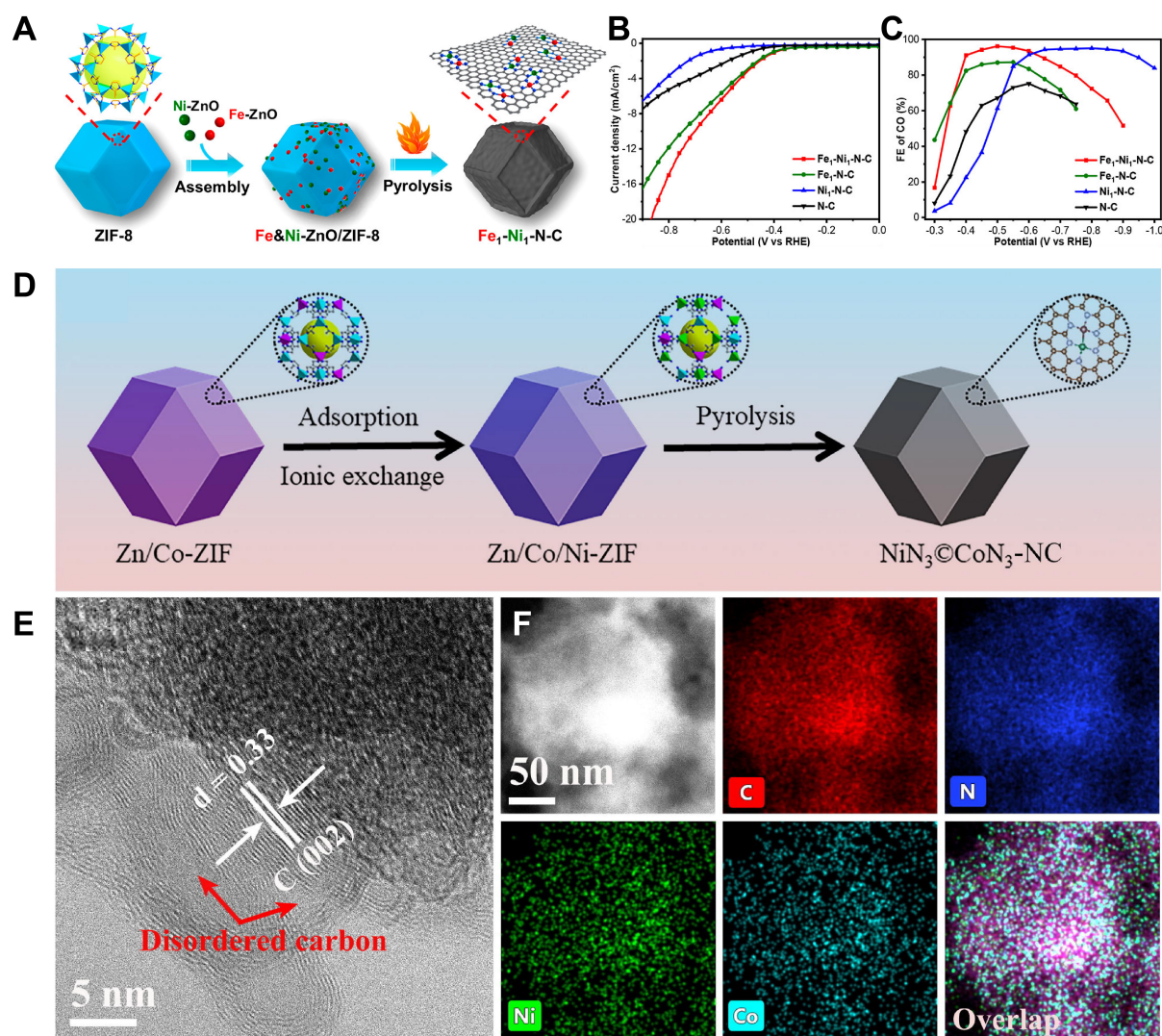


Figure 8. (A) Schematic diagram of fabrication of Fe₁-Ni₁-N-C; (B and C) LSV curves (B) and FE_{CO} test (C) of Fe₁-Ni₁-N-C and other catalysts; (A-C) are quoted with permission from Jiao *et al.* [163]; (D) Preparation strategy of NiN₃@CoN₃-NC; (E and F) HRTEM test (E) and HAADF-STEM elemental mapping images (F) of NiN₃@CoN₃-NC; (D-F) are quoted with permission from Zhang *et al.* [170]. ZIF: Zeolitic imidazolate framework; RHE: reversible hydrogen electrode; LSV: linear sweep voltammetry; FE_{CO}: Faradaic efficiency for CO; HAADF-STEM: high-angle annular dark field scanning transmission electron microscopy.

Additionally, Zhu *et al.* strategically engineered quasi-covalently linked Ni-Cu dual-atomic sites, optimizing the Ni 3d electronic structure to achieve high-efficiency CO₂RR [Figure 9A] [171]. Ni-ZIF-8 was used as the host, with Cu/1,10-phenanthroline as guest; the precursor Ni/Cu-ZIF-8 was generated by a host-guest construction approach. After Ni/Cu-ZIF-8 was pyrolyzed under a flowing Ar/H₂ atmosphere, the final product Ni-Cu dual-atom sites catalyst was got and named Ni/Cu-N-C. CO₂RR performance evaluation showed the Ni/Cu-N-C catalyst exhibited the highest FE_{CO} of 97.7% and turnover frequency (TOF) of 20,695 h⁻¹ at -0.7 V and -0.6 V, respectively, with no significant current decay and remaining unchanged FE_{CO} over 60 h [Figure 9B-D]. Compared with other reference catalysts, Ni/Cu-N-C with heterobimetallic atomic active sites showed the strongest selectivity, highest intrinsic activity and longest stability for CO₂RR. Also using ZIF-8 as a precursor, through a two-stage ligand etching and pyrolysis procedure, Pei *et al.* prepared a heterogeneous DAC on a carbonaceous framework with yolk as the shell coordinated by S and N (Zn₁Mn₁-SNC) [Figure 9E] [147]. The configurations of dual active sites S/N-Zn-Mn-S/N in Zn₁Mn₁-SNC

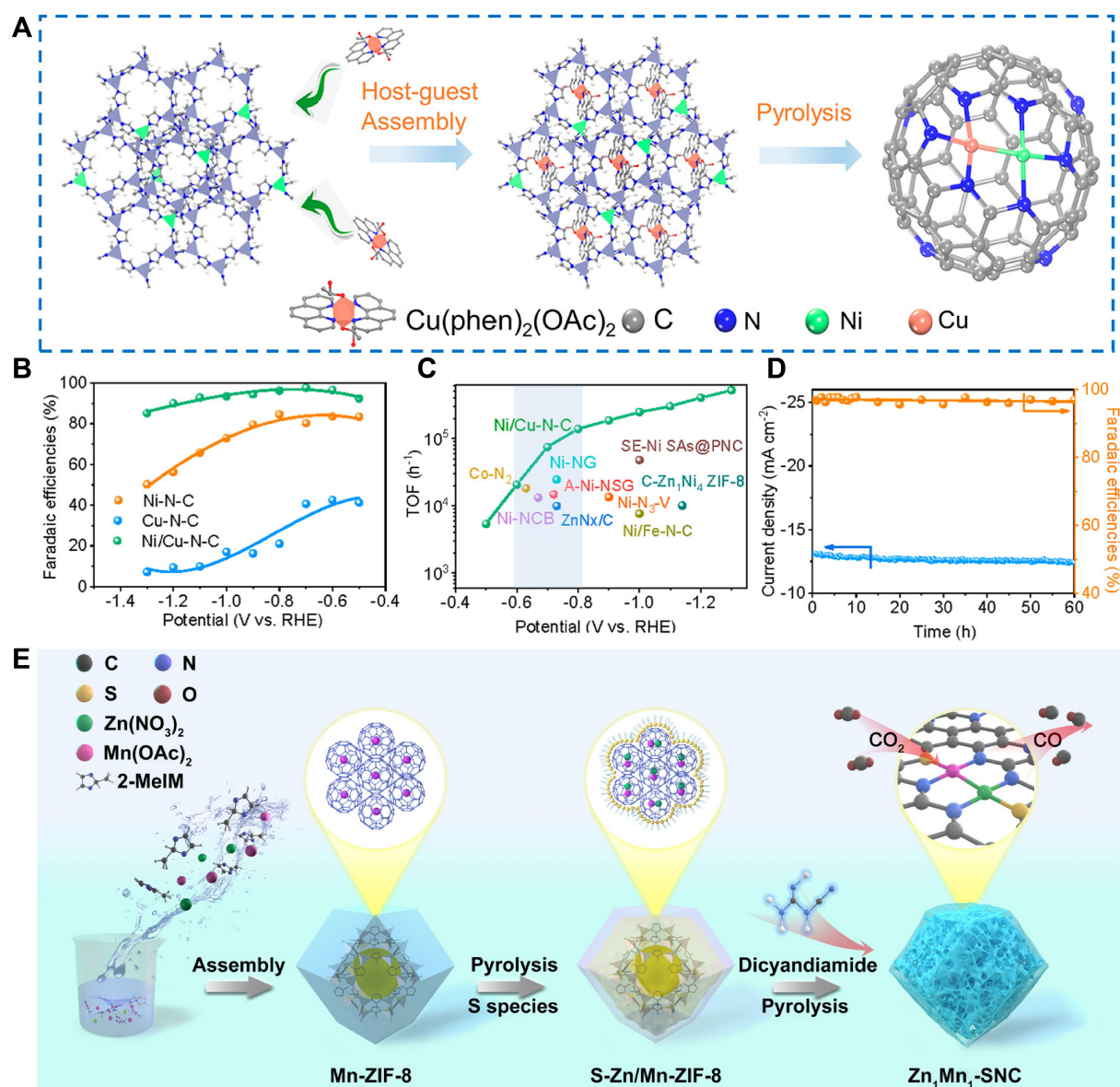


Figure 9. (A) Schematic diagram of fabrication of Ni/Cu-N-C; (B and C) FE_{CO} tests (B) and TOF (C) of Ni/Cu-N-C and other reference catalysts; (D) Current-time response and the corresponding FE_{CO} of Ni/Cu-N-C at -0.7 V; (A-D) are quoted with permission from Zhu et al. [171]; (E) Preparation strategy of Zn₁Mn₁-SNC, quoted with permission from Pei et al. [147]. ZIF: Zeolitic imidazolate framework; RHE: reversible hydrogen electrode; TOF: turnover frequency; FE_{CO}: Faradaic efficiency for CO.

were completely different from the previous active sites structure (more binding with N), making the Zn₁Mn₁-SNC a high-efficiency catalyst for electrochemical conversion of CO₂ to CO.

Characterization of active sites

In MOFs with atomic catalysts, characterization techniques have been essential in identifying the locations of metal active sites, as their distribution and environment have directly influenced catalytic performance [172–174]. Identifying the position of metal active sites aids in understanding the mechanisms of catalytic reactions, thereby optimizing catalyst design [175–177]. Furthermore, different positions of metal sites may exhibit varying selectivity towards reactants, and understanding their locations could enhance the selectivity of the catalyst [178–180]. Additionally, the environment of the metal sites could affect their stability,

and knowing their positions could help predict the catalyst's behavior during the reduction reaction course^[181]. Characterization of the architecture and composition of materials is often performed using various instruments, including HAADF-STEM, powder XRD (PXRD), EDS, synchrotron-based soft X-ray absorption near-edge structure (XANES), X-ray photoelectron spectroscopy (XPS), X-ray absorption spectroscopy (XAS), nuclear magnetic resonance (NMR), electron paramagnetic resonance (EPR), and PXRD^[182]. Additionally, spin-polarized density functional theory (DFT) is used to forecast which sites may exhibit higher catalytic activity^[183].

Electron microscopy techniques and EDS-mapping

HAADF-STEM, TEM, and SEM are used to observe the microstructure, morphology, and elemental distribution of catalysts^[184]. Electron microscopy plays a vital part in examining the active sites of catalysts and their microstructures, studying the elemental distribution and interactions of materials, and revealing the characteristics and behavior of metal sites^[185]. EDS provides qualitative and quantitative information about elements by analyzing the characteristic X-rays emitted from the sample. EDS could analyze the distribution of elements at the nanoscale, revealing the specific locations of metal sites within the MOFs structure^[186].

Wang *et al.* used HAADF-STEM to observe the atomic-level configuration of catalyst (FeSe/NC) during their research, identifying the atomic positions of different elements based on differences in atomic brightness, thereby determining the distribution of metal sites^[187]. A HAADF-STEM image of Fe/ZIF-8, which exhibited a uniform rhombic dodecahedron shape, indicated that Fe ions have been successfully encapsulated within the cage-like structure of ZIF-8, laying the foundation for the subsequent synthesis of FeSe/NC [Figure 10A]. The HRTEM image of FeSe/NC showed that it had a dodecahedron shape [Figure 10B]. From results of HAADF-STEM image of FeSe/NC, it could be seen that many voids appeared within FeSe/NC, which increased the disclosure of Fe sites and contributed to mass diversion during ORR process [Figure 10C]. The EDS mapping images of FeSe/NC further confirmed a homogeneous distribution of Fe, Se, N, and C throughout the catalyst, indicating that these elements work synergistically within the catalyst system, with Fe sites closely interacting with other elements to form the catalytic active center [Figure 10D]. Liu *et al.* analyzed the Fe-Fe bimetallic center catalyst ($\text{Fe}_2\text{N}_6\text{-S}$) within ZIF-8^[188]. The HRTEM image of $\text{Fe}_2\text{N}_6\text{-S}$ visually presented the micro-morphology and crystal structure characteristics of the material, indicating no significant aggregation of metal particles and an amorphous state [Figure 10E]. The HAADF-STEM images of $\text{Fe}_2\text{N}_6\text{-S}$ clearly showed the distribution of Fe, with bright spots formed by higher molecular weight Fe species confirming their uniform dispersion within the graphite carbon and existence of bimetallic sites, revealing the distribution patterns of the metal sites at the microscopic level [Figure 10F and G]. Sun *et al.* researched Cu-Se DACs^[189]. Characterization through EDS image of Cu-Se DACs clearly proved the equal interspersions of copper and selenium atoms in the Cu-Se DACs [Figure 10H]. This observation indicated a similarity in the copper content. Additionally, HAADF-STEM images of Cu-Se DACs proved that the Cu-Se DACs were evenly distributed throughout the carbon matrix [Figure 10I and J].

X-ray absorption fine structure

X-ray absorption fine structure (XAFS) is a highly effective method to detect the local structure of single and dual atoms. XRD has been used to establish the crystalline construction of catalyst, while XPS detects the chemical component and electronic states of catalyst, including the oxidation number and coordination conditions of metallic elements^[190]. Meanwhile, XAS, specifically XANES, has been used to analyze the oxidation number and coordination conditions of metallic elements within the catalyst, while extended XAFS (EXAFS) provides information on the local structure of metallic atoms, determining bond lengths

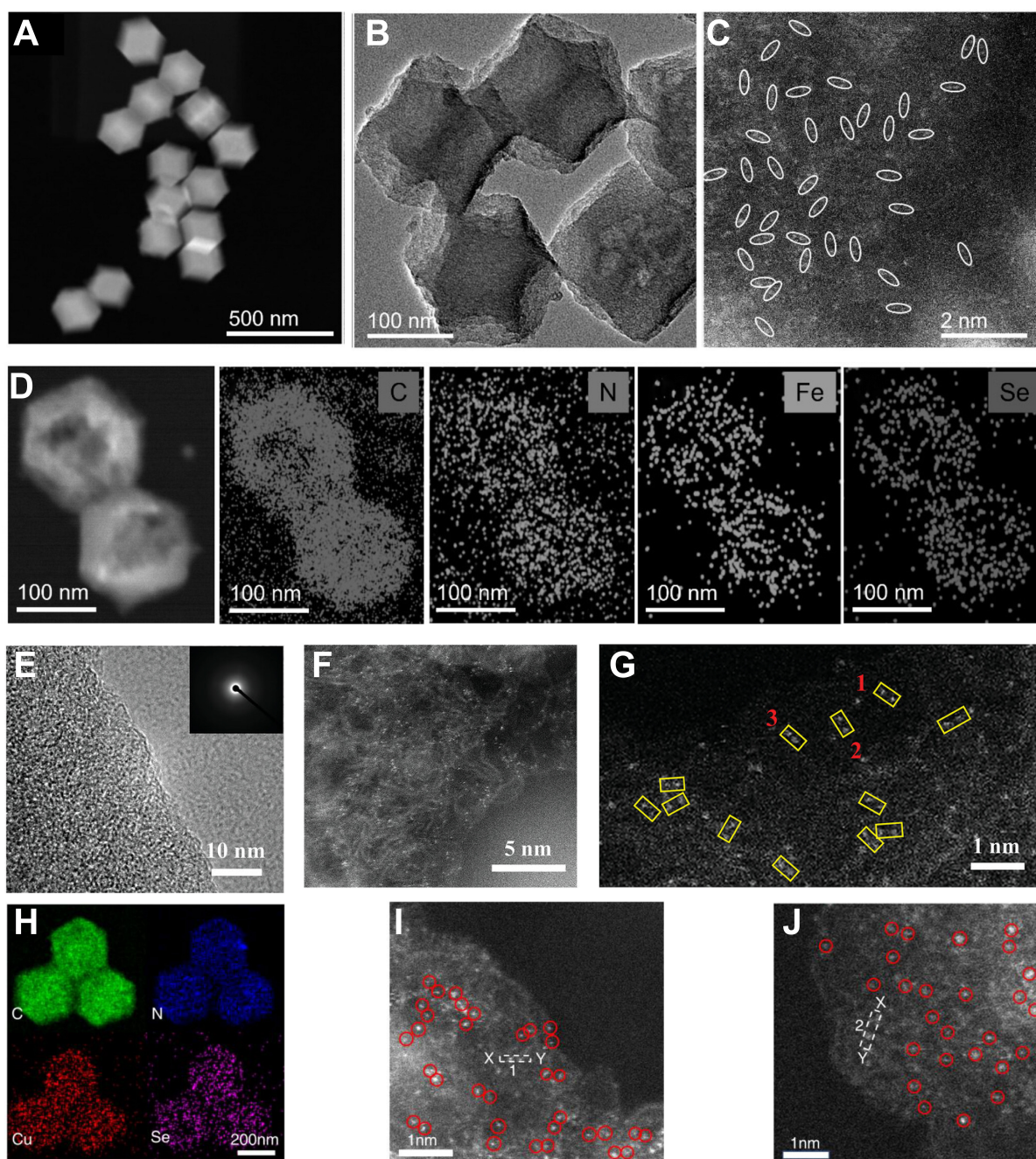


Figure 10. (A) HAADF-STEM of FeSe/NC; (B) HRTEM of FeSe/NC; (C) HAADF-STEM of FeSe/NC; (D) EDS mapping images of FeSe/NC; (A-D) are quoted with permission from Wang *et al.*^[187]; (E) HRTEM image of Fe₂N₆-S (insert was SAED pattern with selective area); (F and G) HAADF-STEM images of Fe₂N₆-S; (E-G) are quoted with permission from Liu *et al.*^[188]; (H) EDS image of Cu-Se DACs; (I and J) HAADF-STEM image of Cu-Se DACs (I) and Cu-Se SACs (J); (H-J) are quoted with permission from Sun *et al.*^[189]. HAADF-STEM: High-angle annular dark field scanning transmission electron microscopy; EDS: energy-dispersive X-ray spectroscopy; HRTEM: high-resolution transmission electron microscopy; DACs: dual-atom catalysts; SACs: single-atom catalysts.

and coordination numbers for metal-ligating atom interactions^[191-193].

Sun *et al.* determined the changes in oxidation states of Ru and Zr elements in Ru₁Zr₁/Co DACs by analyzing their XANES spectra^[194]. The near-edge absorption energy of Ru shifted to smaller values under

H₂ reduction and syngas atmosphere, approaching the absorption energy of Ru foil, indicating a reduction in the oxidation state of Ru atoms [Figure 11A]. In contrast, the near-edge absorption energy of Zr remained similar and close across different stages, suggesting that Zr atoms maintained a positive charge and their oxidation state remained relatively unchanged throughout the reaction process [Figure 11B]. Through EXAFS analysis, a fresh peak appears around 2.4 Å, attributed to Ru-Co or Ru-Ru coordination, suggesting Ru atoms undergoing bond reconstruction in the back of reductive reaction [Figure 11C]. For Zr atoms, a peak associated with Zr-O coordination was found at approximately 1.6 Å in samples at different stages, indicating that Zr atoms primarily maintained Zr-O coordination, being uniformly dispersed in Co nanoparticles and the support, and were difficult to reduce [Figure 11D]. Additionally, Liu *et al.* confirmed the presence of Fe-Cu coordination through the appearance of the Fe-Cu peak in the EXAFS spectra within K-edges of Fe and Cu [Figure 11E]^[195]. The analysis indicated that the metal atoms were in an atomically dispersed state on the FeCu-NC catalyst, with no evidence of Fe-Fe or Cu-Cu scattering. Meanwhile, Zhao *et al.* investigated Ni-Co bimetallic site relay electrocatalysts and found that the structures of the synthesized catalysts (such as Co-MOFs and NiCo-MOFs series) were consistent with the simulated MOFs structure (CCDC no. 1502849) through XRD analysis [Figure 11F]^[196]. Furthermore, XPS analysis revealed a survey spectrum confirming the presence of Ni, Co and N elements in Ni₂Co₁-MOFs, which was consistent with the EDS results [Figure 11G]. Post-fresh electrolysis testing showed the disappearance of the N 1s peak and changes in the oxidation states of Ni and Co, indicating that Ni²⁺/Ni³⁺ and Co²⁺/Co³⁺ participate as redox pairs in the reaction [Figure 11H and I].

DFT calculations

DFT plays a pivotal role in studying atomically dispersed catalysts within MOFs, particularly in characterizing metal active sites. It provides insights into electronic properties, revealing band structures and density of states crucial for understanding catalytic behavior. DFT enables the simulation of potential energy surfaces to identify reaction pathways and transition states, elucidating catalytic mechanisms^[197]. Additionally, it calculates adsorption energies to evaluate how reactants and intermediates interact with metal sites, informing on selectivity and efficiency^[198].

Qiao *et al.* methodically studied the property of a succession of two-dimensional MOFs (M₃(HADQ)₂) as single atomic catalysts used in oxygen reduction reaction (ORR) using DFT method and microkinetic simulations^[199]. A significant linear correlation was found between ΔG_{OH^*} and either ΔG_{OOH^*} or ΔG_{O^*} [Figure 12A], which governed the ORR activity trends across different monolayers. The positioning of the volcano plot allowed for a clear assessment of the relative activity of different metal active sites in the ORR, enabling effective characterization of these sites [Figure 12B]. Additionally, Ming *et al.* conducted the catalytic cycle for CO₂ reduction in Co₂-MOFs(-NH₂), where the catalyst accepted electrons to form Int-1, which subsequently led to the formation of Int-2 upon adsorption [Figure 12C]^[200]. The energy barrier resulting from the DFT calculations clearly demonstrated the free energy changes (ΔG) during various stages of reduction process, such as the constitution of Int-2 and the proton-coupled electron transfer (PCET) stage [Figure 12D]. Meanwhile, Hu *et al.* utilized DFT calculations to intuitively demonstrate the impact of amino groups on the water adsorption capability of the catalyst [Ru₁/UiO-67-X, X represented -H, -*m*-(NH₂)₂, or -*o*-(NH₂)₂], as well as the differences introduced by amino groups positioned at various locations^[201]. The computed adsorption energies of H₂O adsorbed on Ru₁/UiO-67-X showed that the -NH₂ group located closer to the Ru1 site resulted in lower adsorption energy, as shown in Figure 12E. Additionally, the structural simulation results between H₂O and Ru₁/UiO-67-X showed that Ru₁/UiO-67-*o*-(NH₂)₂ was connected to H₂O by three short bonds O-H...O, O-H...N, and O-H...S, while for Ru₁/UiO-67-H and Ru₁/UiO-67-*m*-(NH₂)₂, there was only a long O-H...O [Figure 12F].

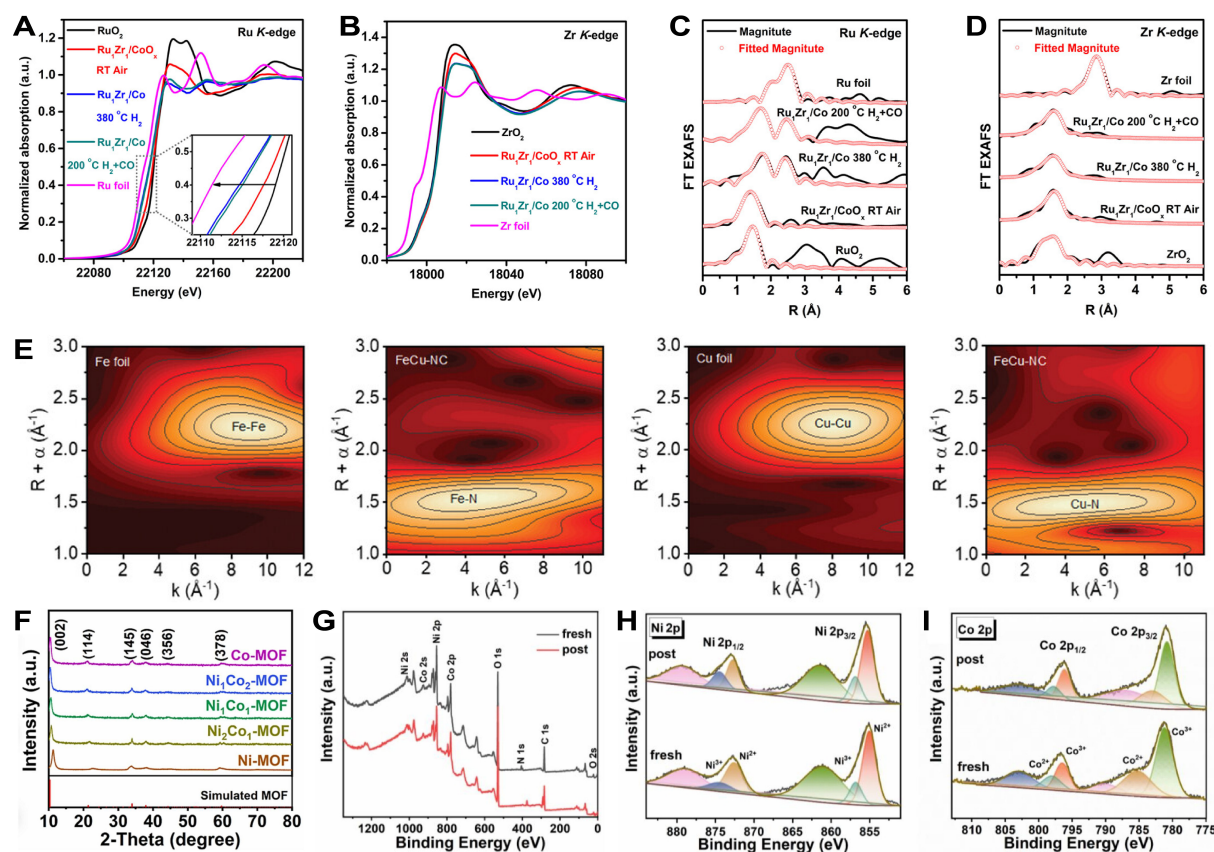


Figure 11. (A and B) Ru K-edge (A) and Zr K-edge (B) XANES spectra of samples under different conditions; (C and D) Ru K-edge (C) and Zr K-edge (D) EXAFS spectra of samples under different conditions; (A-D) are quoted with permission from Sun et al.^[194]; (E) Wavelet-transformed k^3 -weighted EXAFS spectra and corresponding metal foil reference of FeCu-NC, quoted with permission from Liu et al.^[195]; (F) XRD patterns of synthesized MOFs catalysts; (G) XPS spectra of Ni₂Co₁-MOFs; (H and I) High-resolution XPS of Ni 2p (H) and Co 2p (I) of post and fresh Ni₂Co₁-MOFs; (F-I) are quoted with permission from Zhao et al.^[196]. XANES: X-ray absorption near-edge structure; EXAFS: extended X-ray absorption fine structure; XRD: X-ray diffraction; MOFs: metal-organic frameworks; XPS: X-ray photoelectron spectroscopy; FT: Fourier transform.

Overall, for MOFs-based SACs, the main difference is the location and connection of the active metal atoms, such as skeleton-limited, ligand-linked and defect sites. For MOFs-based DACs, the main difference is the type and connection mode of the metal atoms at the two active sites, so there are three types of homologous bimetallic atomic pairs, heterobimetallic isolated atom pairs and heterobimetallic atomic pairs^[202]. In order to have a better understanding of MOFs-based SACs/DACs, we summarized the relevant information of recent studies of them for CO₂RR mentioned in this review [Table 1]. A clear understanding of these types of MOFs-based SACs/DACs can help us to better study the reaction mechanism of catalysts and regulate the activity of catalysts more efficiently^[203]. In addition, HAADF-STEM emphasizes the identification of isolated single and diatomic pairs through multi-regional statistical analysis and atomic-level resolution images, and demonstrates local magnification. EXAFS and XANES can be used to judge the coordination environment. The coordination number of single atom and diatom may be different. Compare the coordination environment differences between SAC and DAC: single atoms usually show a single coordination peak (such as M-N/O), while diatoms may show a double coordination path (such as M-M coordination bonds). DFT can simulate the spectral characteristics of different structures, thus helping to interpret experimental results^[204].

Table 1. Summary of Recent Studies in MOFs-based SACs/DACs for CO₂RR

SACs/DACs	MOFs	Type	Metal sites	Synthetic strategy	Characterization	Ref.
SAC	MNSs	Skeleton limited	Co(Co-N ₄)	Surfactant-stabilized coordination strategy	HAADF-STEM, EXAFS, XANES, XPS	[103]
SAC	ZIF-8	Skeleton limited	Fe, Ni, Mn, Co, Cu(M-N)	Pyrolysis	HAADF-STEM, XPS	[104]
SAC	PCN-222	Skeleton limited	Cu (Zr ⁴⁺ -O ²⁻ (-Cu ²⁺) and Zr ⁴⁺ -Cu ²⁺)	Ion exchange	XPS, EXAFS, XANES, DRIFTS	[105]
SAC	UiO-67	Ligands regulated	Cu(Cu-C, Cu-O)	MOF encapsulation	HAADF-STEM, XAS, NMR, XPS	[118]
SAC	UiO-67	Ligands regulated	Co(Co-N ₃)	Post-synthetic modification	XPS, XANES, EXAFS, PXRD	[119]
SAC	Ni-MOF-74	Ligands regulated	Ni(Ni-O)	Solvothermal modulation	PXRD, XPS, HAADF-STEM	[120]
SAC	ZIF-67@ZIF-8	Defect engineering regulated	Co(Co-S)	MOF-on-MOF	XPS, HRTEM, XRD	[132]
SAC	UiO-66	Defect engineering regulated	Fe, Cu(M-OH, M-OH ₂)	Solvothermal method	PXRD, EXAFS, HAADF-STEM, XANES	[133]
SAC	Ni-ZIF-8	Defect engineering regulated	Ni(Ni-N ₄)	Microwave-Assisted	HAADF-STEM, XANES, EXAFS, XPS	[134]
DAC	Fe-ZIF-8	Homologous bimetallic	Fe-Fe(Fe ₂ -N ₆)	Template-assisted protocol with H ₂ pyrolysis conditions	HAADF-STEM, EXAFS, XANES, XPS	[158]
DAC	Fe-ZIF-8	Homologous bimetallic	Fe-Fe(Fe ₂ -N ₆)	Precursor encapsulation, pyrolysis	HAADF-STEM, XANES, EXAFS	[159]
DAC	ZIF-8	Heterobimetallic isolated	Fe, Ni(Fe-N ₄ Ni-N ₄)	Mechanochemical methods, pyrolyzed	HAADF-STEM, XANES, EXAFS, XPS	[163]
DAC	Zn/Co-ZIFs	Heterobimetallic	Ni-Co(NiN ₃ CoN ₃)	Pyrolysis	HAADF-STEM, XANES, EXAFS, XRD, XPS	[170]
DAC	Ni-ZIF-8	Heterobimetallic	Ni, Cu(Ni-Cu-N ₆)	Pyrolysis	HAADF-STEM, XANES, EXAFS, XPS, XAS, EDS	[171]
DAC	ZIF-8	Heterobimetallic	Zn, Mn(S/N-Zn-Mn-S/N)	Two-step ligand etch-pyrolysis protocol	HAADF-STEM, EXAFS, XANES, XPS, EDS	[147]
DAC	ZIF-8	Heterobimetallic	Fe-Se(Fe-N, Fe-Se)	Grind, pyrolysis	HAADF-STEM, XANES, EXAFS, XPS, EDS	[187]
DAC	ZIF-8	Homologous bimetallic	Fe-Fe(Fe ₂ N ₆)	Host-guest encapsulation strategy	HAADF-STEM, XANES, XPS	[188]
DAC	ZIF-8	Heterobimetallic	Cu-Se(Cu-N ₄ , Se-C ₃)	Co-pyrolysis	XPS, XANES, EXAFS, HAADF-STEM, EDS	[189]
DAC	ZIF-67	Heterobimetallic	Ni, Co(Ni ²⁺ /Ni ³⁺ Co ²⁺ /Co ³⁺)	Solvothermal method	XPS, TEM, HAADF-STEM, EDS, XRD, FTIR	[196]
DAC	MOF-69C	Heterobimetallic isolated	Ru, Zr(surface of Co NPs)	Solvothermal method	HAADF-STEM, EDS, XPS, XANES, EXAFS	[194]
DAC	IISERP-MOF27	Heterobimetallic	Fe, Cu(FeN ₃ O-Cu N ₄)	Pyrolysis	HAADF-STEM, XANES, EXAFS, XPS	[195]
SAC	2D M3(HADQ)2	Skeleton limited	Co, Cr, Cu, Fe, Mn, Ni, Pd, Rh and Ru(M-N ₄)	Solvothermal synthesis	DFT	[199]
DAC	MOF-(NH2)	Homologous bimetallic	Co(Co-L1-Co)	Mechanochemical methods	PXRD, HRTEM, EDS, XPS, DFT	[200]
SAC	UiO-67-X	Skeleton limited	Ru(Ru-O, Ru-S)	Microwave assisted methods	HAADF-STEM, XANES, EXAFS, DRIFTS	[201]

SACs/DACs: Single/dual-atom catalysts; MOFs: metal-organic frameworks; MNSs: metal-nitrogen supramolecular structure; HAADF-STEM: high-angle annular dark field scanning transmission electron; EXAFS: extended X-ray absorption fine structure; XANES: X-ray absorption near-edge structure; XPS: X-ray photoelectron spectroscopy; ZIF: zeolitic imidazolate framework; PCN: porous coordination network; MOF: metal-organic framework; DRIFTS: diffuse reflectance infrared fourier transform spectroscopy; XAS: X-ray absorption spectroscopy; NMR: nuclear magnetic resonance; PXRD: powder X-ray diffraction; HRTEM: high resolution transmission electron microscopy; XRD: X-ray diffraction; DAC: dual-atom catalyst; EDS: energy-dispersive X-ray spectroscopy; TEM: transmission electron microscopy; FTIR: Fourier transform infrared spectroscopy; IISERP: Indian Institute of Science Education and Research Pune; DFT: density functional theory.

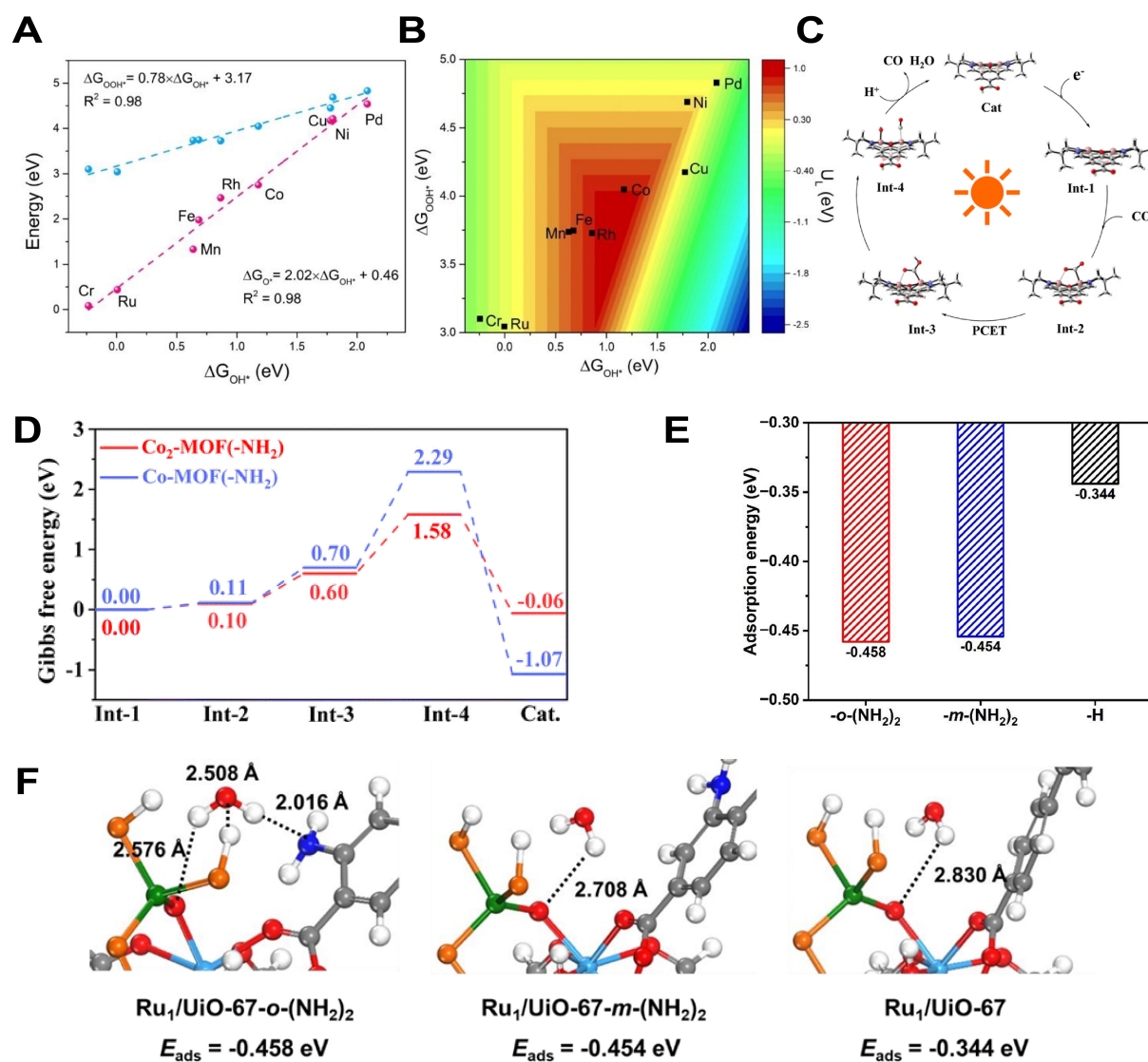


Figure 12. (A) The linear relationships between ΔG_{OOH^+} , ΔG_{O^-} , and ΔG_{OH^+} on different monolayers of 2D MOFs; (B) Changing of ORR catalytic activity with ΔG_{OOH^+} and ΔG_{OH^+} of the 2D MOFs monolayers; (A and B) are quoted with permission from Qiao et al.^[199]; (C) Catalytic cycle for CO_2 reduction in $\text{Co}_2\text{-MOFs}(-\text{NH}_2)$; (D) DFT calculations of energy barriers for $\text{Co}_2\text{-MOFs}(-\text{NH}_2)$ and $\text{Co-MOFs}(-\text{NH}_2)$; (C and D) are quoted with permission from Ming et al.^[200]; (E) The computed adsorption energies of H_2O adsorbed on $\text{Ru}_1/\text{UiO-67-X}$; (E and F) are quoted with permission from Hu et al.^[201]. PCET: Proton-coupled electron transfer; Cat: catalyst; Int: intermediate; MOFs: metal-organic frameworks; ORR: oxygen reduction reaction; DFT: density functional theory.

CATALYTIC MECHANISM OF ACTIVE SITES IN CO_2RR

Various strategies have been employed to reduce CO_2 to usable chemicals, such as photocatalysis, electrocatalysis, thermal catalysis, biological reduction, and various co-catalytic methods^[205-207]. Electrochemical and photochemical catalytic CO_2RR are considered two very promising strategies because they are capable of converting CO_2 under ambient temperature and pressure conditions^[118,208,209]. Electrocatalytic and photocatalytic CO_2RR use different energies: electrocatalysis reduces CO_2 by stimulating electron movement through current and voltage, while photocatalysis absorbs light energy to stimulate highly active photoelectrons to realize CO_2 under light irradiation^[210-212]. Although the common

goal of both is to activate CO₂ molecules by catalyzing energy conversion at the active sites, the CO₂RR of whether electrocatalyzed or photocatalyzed, is quite complex^[213]. Therefore, to achieve efficient catalytic reduction of CO₂, understanding the mechanism of electrocatalytic and photocatalytic CO₂RR is a very basic and key problem. In addition, the relationship between active sites and catalytic efficiency should be deeply understood.

Mechanism of electrocatalytic CO₂RR

The ECRR has the advantages of strong controllability, adjustable electrochemical parameters and high conversion efficiency under voltage drive^[214–216]. However, this CO₂RR process encompasses several electron and proton transfer stages and requires overcoming the high overpotential brought by the thermodynamic and kinetic obstacles caused by the stability of the CO₂ molecule^[217,218]. Therefore, a low overpotential means a low electrolytic potential, resulting in a high current density and Faraday efficiency, achieving a high catalytic rate^[219,220]. ECRR is performed at the electrode/electrolyte interface, where MOFs could be used as both electrode and electrocatalyst, and the materials with similar structure to graphene derived from MOFs by pyrolysis have good conductivity^[221,222]. Metal centers such as Fe, Co, Ni, *etc.* and their assembly serve as atomic-level catalytic sites within MOFs that could promote the efficiency of CO₂ adsorption and activation^[223–225]. Meanwhile, organic ligands could modify the electron atmosphere of the metallic ion and provide additional proton transfer sites, immobilizing the intermediate product of the reaction^[226,227]. Moreover, the porous structure of MOFs offers an extensive surface area, enhancing the mass transfer of CO₂ and intermediates. The pore dimensions and morphology of MOFs could be adjusted to optimize both adsorption and diffusion processes^[228,229].

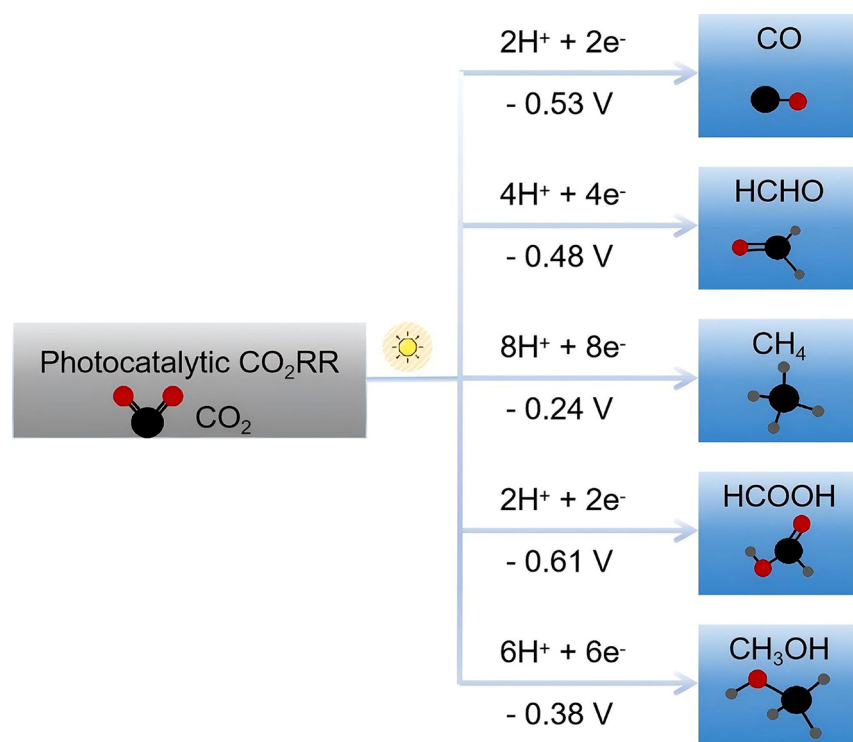
In MOFs-based SACs/DACs, the CO₂RR typically encompasses several stages, during which protons and electrons are transferred simultaneously, resulting in the generation of a variety of products^[70,230]. With the difference in the number of electrons transferred during CO₂ reduction, these products could be divided into C1 (CO, HCHO, CH₄, HCOOH and CH₃OH) and C2 (C₂H₄, C₂H₅OH and CH₃COOH) according to the number of carbon atoms. The products and their corresponding reaction equations are listed in Table 2^[122]. For MOFs-based SACs/DACs, adjusting their geometric and electronic structure, especially the configuration of atomic active sites, could effectively stimulate the activation of CO₂ molecules and promote these CO₂RR^[231]. Moreover, with appropriate interactions, the atomic active sites could be combined with the intermediates, thus avoiding competitive hydrogen evolution reactions^[232]. Studies have shown that the active sites in atomic-level catalysts are isolated from each other compared to non-atomic-level catalysts; the activation of CO₂ molecules also occurs at isolated locations of the active sites^[233]. Therefore, the adsorption of H₂O molecules to isolated sites is inhibited in atomic-level catalysts, and the generation of hydrogen evolution reaction is completely limited^[234].

Mechanism of photocatalytic CO₂RR

Generally, the process of CO₂RR conversion is divided into three steps: (1) adsorption of CO₂; (2) transportation of carriers and electrons; and (3) activation of CO₂. For photocatalytic CO₂RR, the third step is the key^[235]. From the dynamic process of reduction reaction, the process of photocatalytic CO₂RR is similar to electrocatalysis, involving multi-electron reactions that break multiple chemical bonds, and the reaction equations are the same^[236,237]. However, the products of photocatalytic CO₂RR are not as many as electrocatalysis, almost C1 products (CO, HCHO, CH₄, HCOOH and CH₃OH) [Figure 13]^[238,239]. As mentioned above, the activation barrier due to the stability of CO₂ requires an energy of 750 kJ/mol to break the C–O bond, meaning that a catalyst needs to absorb enough light energy and convert it into electron-hole pairs which determines the photocatalytic activity^[240–242]. Therefore, the activity of photocatalyst could be significantly enhanced by broadening the wavelength range and increasing, improving the light absorption efficiency, and stimulating the separation of electrons and holes from each other^[243].

Table 2. Products and corresponding reaction equations of electrocatalytic CO₂RR

C1 or C2	Products	Reaction equations
C1	Carbon monoxide (CO)	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{CO} + \text{H}_2\text{O}$
	Formaldehyde (HCHO)	$\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$
	Methane (CH ₄)	$\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$
	Formic acid (HCOOH)	$\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- \rightarrow \text{HCOOH}$
C2	Methanol (CH ₃ OH)	$\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$
	Ethylene (C ₂ H ₄)	$\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{CH}_4 + 4\text{H}_2\text{O}$
	Ethanol (C ₂ H ₅ OH)	$\text{CO}_2 + 12\text{H}^+ + 12\text{e}^- \rightarrow \text{C}_2\text{H}_5\text{OH} + 3\text{H}_2\text{O}$
	Acetic acid (CH ₃ COOH)	$2\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- \rightarrow \text{CH}_3\text{COOH} + 2\text{H}_2\text{O}$

CO₂RR: CO₂ reduction reaction.**Figure 13.** Products and reaction conditions of photocatalytic CO₂RR. CO₂RR: CO₂ reduction reaction.

The conjugated pi-system of MOFs could absorb additional photons and promote photochemical reactions, while its porous structure is conducive to surface adsorption of the active sites with more CO₂ molecules captured^[244]. Therefore, MOFs materials could improve the activity of photocatalytic CO₂RR to a certain extent. However, the conversion efficiency of MOFs-based photocatalytic CO₂RR has not been as efficient as expected^[245,246]. Combined with the atomic active sites and their diverse electronic and coordination structures, MOFs-based SACs/DACs have more selectivity and higher catalytic activity for photocatalytic CO₂RR^[247]. Combining the dual advantages of MOFs and atomic-level catalysts and overcoming the disadvantages of other homogeneous and heterogeneous catalysts, MOFs-based SACs/DACs have become one of the important members in photocatalytic CO₂RR^[248].

Relationship between active sites and catalytic efficiency

From the analysis of catalytic mechanism of active sites in CO₂RR above, whether photocatalysis or electrocatalysis, the active sites are the key to determining the activation of CO₂ molecules and the final catalytic performance^[249]. Thus, it is particularly important to understand the relationship between active sites and catalytic efficiency. For MOFs-based SACs/DACs, the actual catalytic active sites are mainly determined by the coordination effect^[81,250].

On the one hand, regulating the coordination N atom is the key factor that directly determines the synergies between metal active sites and carriers, and even the overall catalytic efficiency. On common N-doped carbon-based carriers, metal atom generally forms 4-coordinated active sites (M-N_xC_y)^[251]. A decrease in the coordination saturation of the metallic active centers leads to a reduction in its coordination number, thereby enhancing the likelihood of interaction with the matrix, and resulting in better catalytic performance^[252,253]. In addition, the unsaturated coordination of M-N_x (x < 4) site is more favorable to electron transfer in the catalytic process due to the vacancy defect^[254,255]. Therefore, by establishing multi-vacancy, the unsaturation of the metallic active atoms could be improved with the reduction of coordination, thus enhancing the catalytic activity. On the other hand, the electronic structure of M-N₄ could be changed through the incorporation of heterogeneous atoms (P, S, or B). Through the doping or substitution of heterologous atoms, the original coordination structure of M-N₄ will produce a reconstruction of the local coordination environment, and the coordination atoms could transfer more dynamic electrons to the metal center, so enhancing the catalytic efficiency^[256].

APPLICATIONS OF MOFS-BASED SACS/DACS DESIGNED BASED ON ACTIVE SITES IN CO₂RR

MOFs-based materials and their derivatives provide more selectivity in creating highly active SACs and DACs^[257,258]. Investigators could leverage their innovative thinking and creativity to build MOFs-based SACs/DACs featuring diverse structural configurations and performance for electrocatalytic and photocatalytic CO₂RR^[259-261].

Electrocatalytic CO₂RR

ECRR offers greater controllability and flexibility, allowing for the adjustment of current density and potential to precisely control the reaction rate and product selectivity^[262-264]. For MOFs-based SACs/DACs used in ECRR, synergistic effects and coordination conditions of single/dual-atom active sites, as well as fine-tuning of preparation conditions, will result in different catalytic activities^[265,266].

Here in a MOFs-based SAC, the coordination environment of single-atom nickel significantly influenced its electrocatalytic performance in CO₂ reduction. Gong *et al.* anchored Ni atoms within nitrogen-doped porous carbon, forming active sites with different Ni-N coordination structures and quantity, such as Ni_{SA}-N₄-C (4.0), Ni_{SA}-N₃-C (3.4), and Ni_{SA}-N₂-C (2), respectively [Figure 14A]^[267]. Result of electrocatalytic CO₂ reduction reaction showed that Ni_{SA}-N₂-C exhibited a top FE_{CO} of 98% at 0.8 V, demonstrating a best catalytic efficiency of Ni_{SA}-N₂-C in ECRR among all measured SACs [Figure 14B]. Furthermore, the TOF for CO production from Ni_{SA}-N₂-C reached 1,622 h⁻¹ at 0.8 V and increased to 3,467 h⁻¹ at 1.0 V, significantly surpassing that of Ni_{SA}-N₄-C and Ni_{SA}-N₃-C, thus demonstrating enhanced catalytic activity [Figure 14C]. Peng *et al.* developed single-atom Ni catalysts (Ni₁-N-C(X), where X = Cl, Br, I) based on ZIF-8 using a strategy for modifying metal halides post-synthesis^[268]. EXAFS fitting revealed that the coordination environment of Ni atoms consisted of four nitrogen atoms in the plane and one chlorine atom in an axial position, successfully anchored onto the N-doped carbon support with a specific coordination structure [Figure 14D]. Regarding electrocatalytic CO₂ reduction performance, Ni₁-N-C(Cl) achieved a highest FE of

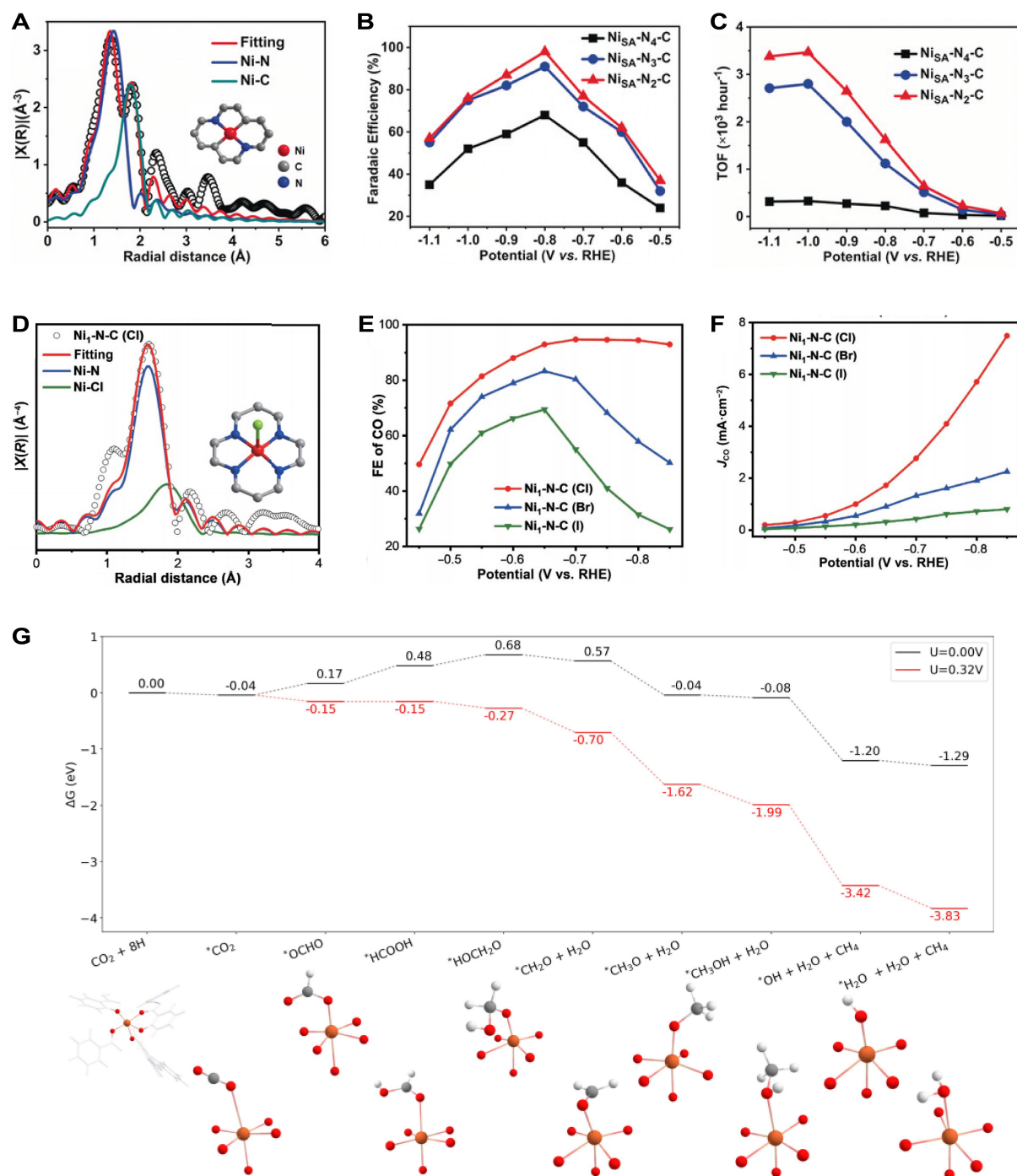


Figure 14. (A) EXAFS fitting and structural model of Ni_{SA}-N₂-C; (B and C) FE_{CO} (B) and corresponding TOFs of CO (C) of Ni_{SA}-N_X-C; (A-C) are quoted with permission from Gong *et al.* [267]; (D) EXAFS fitting and structural model of Ni₁-N-C (Cl); (E and F) FE_{CO} (E) and J_{CO} (F) over Ni₁-N-C(X); D-F are quoted with permission from Peng *et al.* [268]; (G) Schematic diagram of free energy change (top) and structural change (bottom) of Fe-MOFs-74 in CO₂RR, quoted with permission from McCarver *et al.* [269]. TOF: Turnover frequency; RHE: reversible hydrogen electrode; FE_{CO}: Faradaic efficiency for CO; EXAFS: extended X-ray absorption fine structure; MOFs: metal-organic frameworks.

94.7% for CO production at -0.7 V, significantly surpassing that of Ni₁-N-C(Br) and Ni₁-N-C(I) [Figure 14E]. Additionally, the CO partial current density of Ni₁-N-C(Cl) also outperformed that of two

other samples [Figure 14F]. McCarver *et al.* employed first-principles calculations to investigate Fe-MOFs-74 for CO₂ reduction^[269]. Result of schematic diagram of structural change of Fe-MOFs-74 showed that Fe atoms were fixed at specific sites within the MOFs-74 framework as catalysts [Figure 14G]. At a potential of 0.32 eV, the transition from *OCHO to *HCOOH reached a state of equal energy, rendering the reaction feasible and ultimately favoring the selective production of CH₄ without binding to the Fe sites.

With fine-tuning of preparation conditions, Lim *et al.* synthesized and pyrolyzed Ni ZIF-8 via a solution method to prepare pyrrolic nitrogen-stabilized Ni SACs (Ni SAC-800 and Ni SAC-1000) with low-coordination Ni-N_x sites [Figure 15A]^[270]. EXAFS analysis revealed the presence of a Ni-N peak without a Ni-Ni peak, indicating that the Ni atoms were distributed as isolated atoms throughout the carbon matrix within Ni SAC [Figure 15B]. The FE_{CO} of Ni SAC significantly changed with increasing pyrolysis temperature, showing a 40.76% FE_{CO} of Ni SAC-800 and a 98.24% FE_{CO} of Ni SAC-1000 at -0.8 V RHE, respectively [Figure 15C]. Meanwhile, Ni SAC-1000 demonstrated exceptional CO partial current density (*J*_{CO}) at various potentials, reaching the top 148.25 mA·cm⁻² at -1.4 V RHE and significantly outperforming other samples [Figure 15D]. Song *et al.* prepared Cu SAC materials with different asymmetrical atomic interfaces, specifically CuN₃O/C and CuCO₃/C, using a pyrolysis method based on Cu/Zn-MOFs-74 precursors, as illustrated in Figure 15E^[271]. Results of FT-EXAFS showed that the central copper atom was surrounded by three nitrogen atoms and one oxygen atom in its coordination environment for CuN₃O/C [Figure 15F]. The LSV curve of CuN₃O/C indicated a higher current density compared to CuN₃O/C, suggesting better activity [Figure 15G]. The FE_{CO} of CuN₃O/C could reach 96% at -0.8 V [Figure 15H]. The TOF value was as high as 2,782.6 h⁻¹ at -0.9 V vs. RHE, demonstrating that CuN₃O/C exhibited high activity, selectivity, and efficient catalytic performance in the ECRR [Figure 15I].

Besides MOFs-based SACs, MOFs-based DACs were used a lot for ECRR. Feng *et al.* *in situ* doped Cu²⁺ and Fe(acac)₃ molecules into ZIF-8 and prepared a Fe/Cu-N-C catalyst through pyrolysis under Ar gas flow^[272]. The coordination structure of Fe/Cu-N-C was identified as N₄Fe-CuN₃, reflecting the existence of coordination between Fe atoms and N atoms, along with a specific bonding relationship with Cu atoms, featuring an average bond distance of approximately 2.01 Å [Figure 16A]. The FE_{CO} values for Fe/Cu-N-C were above 95% in the potential range of 0.4-1.1 V and peaked at nearly 99% when the potential was 0.8 V, far higher than those of other reference catalysts [Figure 16B]. Meanwhile, the TOF of Fe/Cu-N-C was 5,047 h⁻¹ at 1.1 V, significantly surpassing that of Fe-N-C and Cu-N-C [Figure 16C]. Sun *et al.* prepared a dual atomic sites Ru₁Zr₁/Co catalyst (DASC) featuring Ru and Zr via solvothermal and pyrolysis methods^[194]. EDS analysis showed an equable dispersion of Ru (blue) and Zr (green) atoms within Ru₁Zr₁/Co catalyst [Figure 16D]. The TOF of the Ru₁Zr₁/Co catalyst reached as high as 3.8 × 10⁻² s⁻¹, representing a significant enhancement compared to 0.8 × 10⁻² s⁻¹ for Co NPs, 1.4 × 10⁻² s⁻¹ for Zr₁/Co, and 2.7 × 10⁻² s⁻¹ for Ru₁/Co [Figure 16E]. Meanwhile, C_s⁺ selectivity of Ru₁Zr₁/Co could reach 80.7% and far surpassed that of other catalysts [Figure 16E]. Zhang *et al.* prepared Cu/Ni-NC DACs that atomically distributed Ni atoms and Cu atoms embedded in hollow N-doped carbon via a pre-growth-pyrolysis method^[151]. In acidic electrolyte, the EF_{CO} of Cu/Ni-NC exhibited high values over a wide potential range, reaching a top of 99.1% at -1.1 V, outperforming that of Ni-NC and Cu-NC [Figure 16F]. Meanwhile, Cu/Ni-NC exhibited high EF_{CO} in alkaline electrolyte [Figure 16G], with similar result showing in neutral electrolyte [Figure 16H], further confirming the catalytic efficiency advantage of Cu/Ni-NC within reduction of CO₂ to CO under various pH conditions. The performance of the Cu/Ni-NC in terms of CO₂ utilization efficiency was evaluated across different CO₂ flow rates in acidic and alkaline surroundings with 64.3% for acidic and approximately twice for alkaline, indicating the significant role of Cu/Ni-NC in enhancing CO₂ utilization efficiency in acidic environments [Figure 16I].

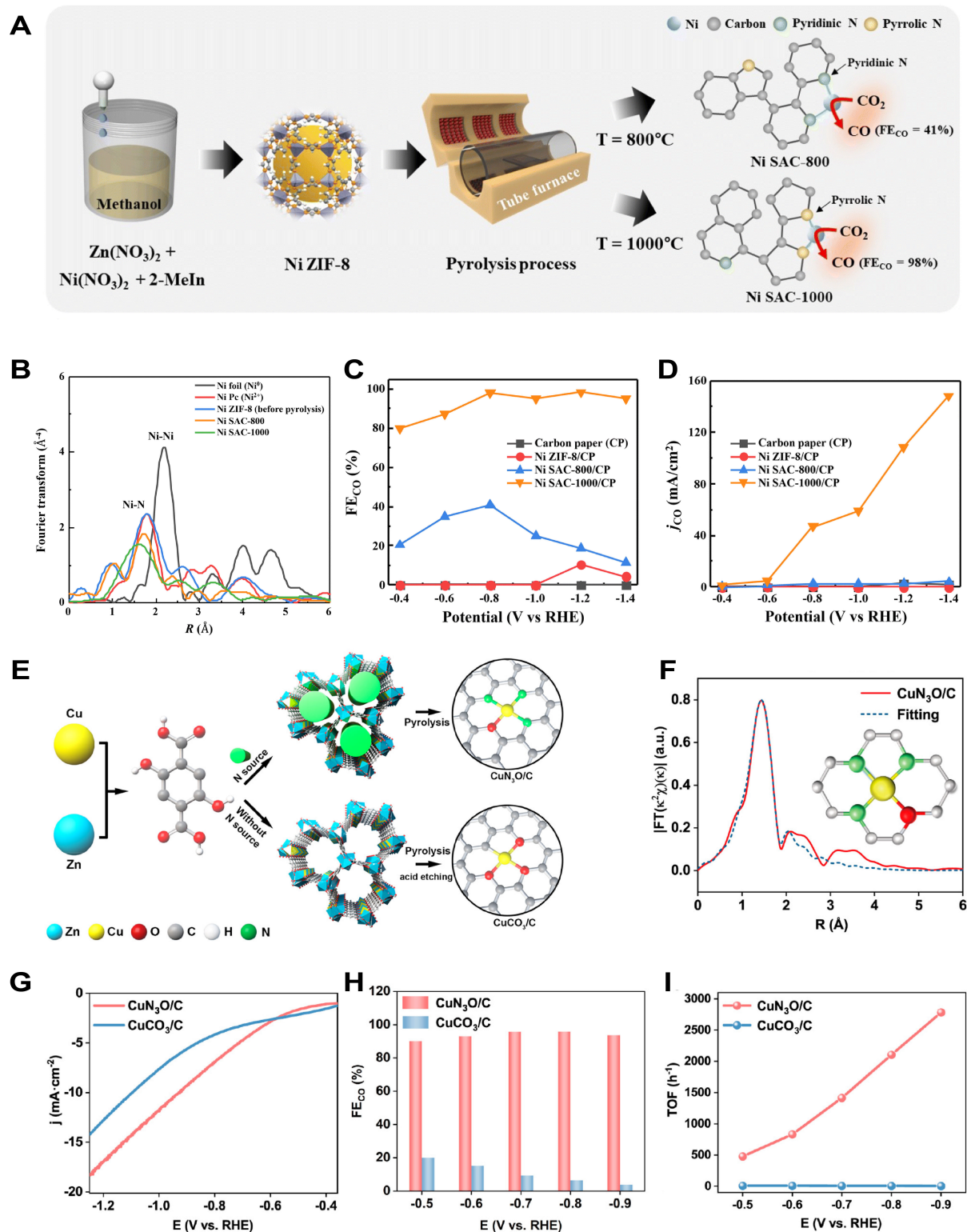


Figure 15. (A) Preparation process and active site diagram of Ni SAC-800 and Ni SAC-1000; (B) FT-EXAFS spectra of the Ni K-edge for Ni-based catalysts; (C and D) FE_{CO} (C) and j_{CO} (D) over Ni-based catalysts; (A-D) are quoted with permission from Lim et al.^[270]; (E) Preparation process diagram of CuN_3O/C and $CuCO_3/C$; (F) FT-EXAFS fitting and structural model of CuN_3O/C ; (G-I) LSV curves (G), FE_{CO} (H) and TOFs of CO (I) over CuN_3O/C and $CuCO_3/C$; (E-I) are quoted with permission from Song et al.^[271]. RHE: Reversible hydrogen electrode; ZIF: zeolitic imidazolate framework; FE_{CO} : Faradaic efficiency for CO; SAC: single-atom catalyst; TOF: turnover

frequency; FT: Fourier transform; EXAFS: extended X-ray absorption fine structure; LSV: linear sweep voltammetry.

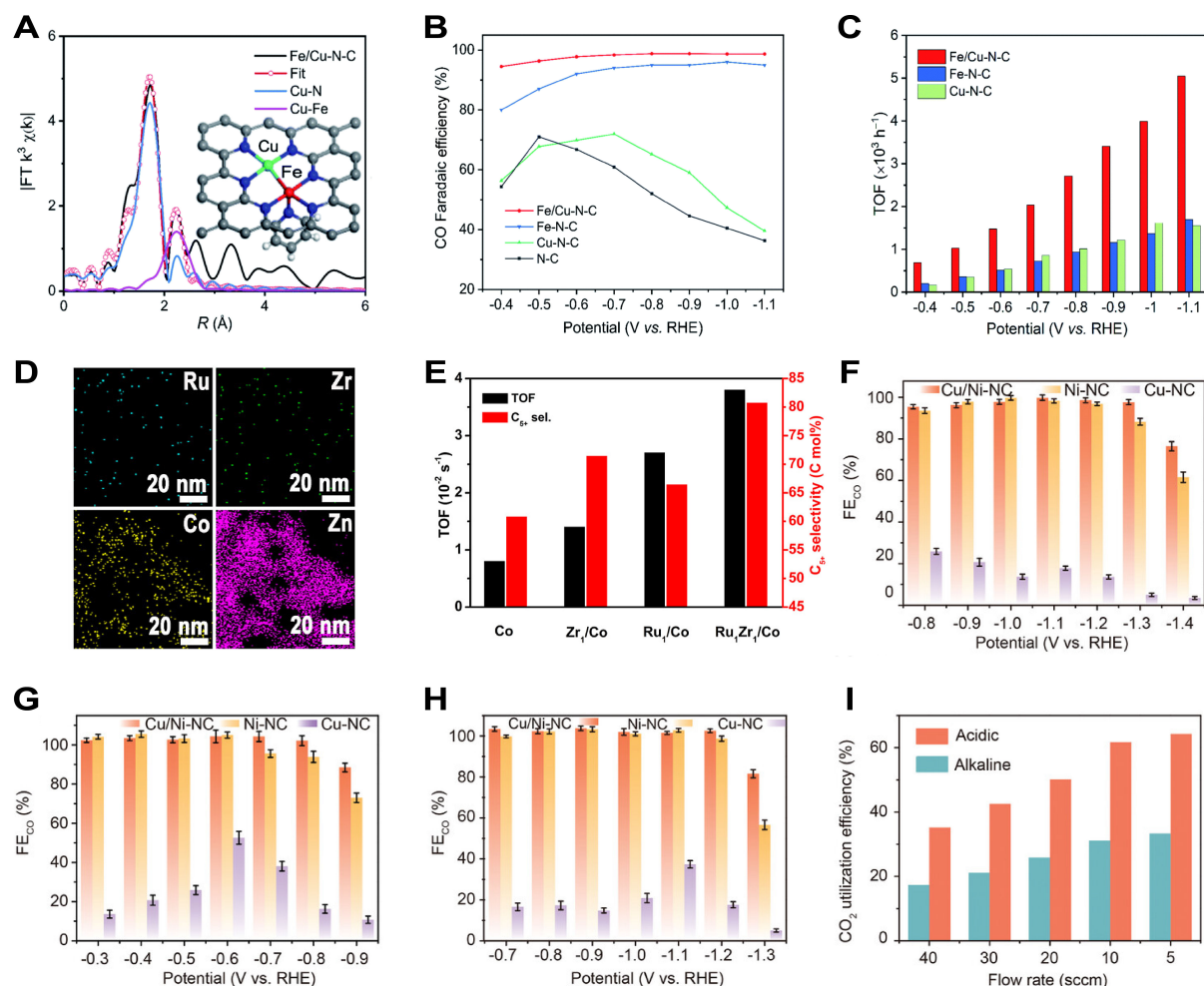


Figure 16. (A) EXAFS fitting and structural model of Fe/Cu-N-C catalyst; (B and C) FE_{CO} (B) and TOFs of CO (C) over different N-C catalysts; (A-C) are quoted with permission from Feng *et al.* [272]; (D) EDS mapping of Ru,Zr/Co catalyst; (E) TOF and C_{5+} selectivity of four Co-containing catalysts; (D and E) are quoted with permission from Sun *et al.* [194]; (F-H) FE_{CO} of Cu/Ni-NC, Ni-NC, and Cu-NC in different electrolytes: acidic (F), alkaline (G), and neutral (H); (I) CO_2 utilization efficiency of Cu/Ni-NC catalyst in acidic and alkaline electrolyte; (F-I) are quoted with permission from Zhang *et al.* [151]. FT: Fourier transform; TOF: turnover frequency; FE_{CO} : Faradaic efficiency for CO; EXAFS: extended X-ray absorption fine structure; EDS: energy-dispersive X-ray spectroscopy.

Photocatalytic CO_2 RR

Photocatalysis is a light-driven chemical reaction that exhibits green, environmentally friendly, and efficient characteristics in CO_2 RR. MOFs-based SACs/DACs have more selectivity and higher catalytic activity for photocatalytic CO_2 RR with controllable active sites and coordination environment [150,273].

For MOFs-based SACs, Liu *et al.* prepared Ni single-atom fixed ZIF-8 catalysts (Ni/SOM-ZIF-8) featuring an organized hierarchical structure of macro and micro pores via pyrolysis for photocatalytic CO_2 RR [274]. EXAFS spectrum of Ni/SOM-ZIF-8 exhibited no characteristic peak for Ni–Ni bonding in R space, and the main peak corresponded to Ni–N bonding (1.43 Å) [Figure 17A]. In terms of photocatalytic CO_2 RR performance, Ni/SOM-ZIF-8 exhibited the best performance, achieving a CO yield of 11.44 m·mol g^{-1} after four hours, which was 44 times and 22 times that of ZIF-8 and SOM-ZIF-8, respectively, and showing high

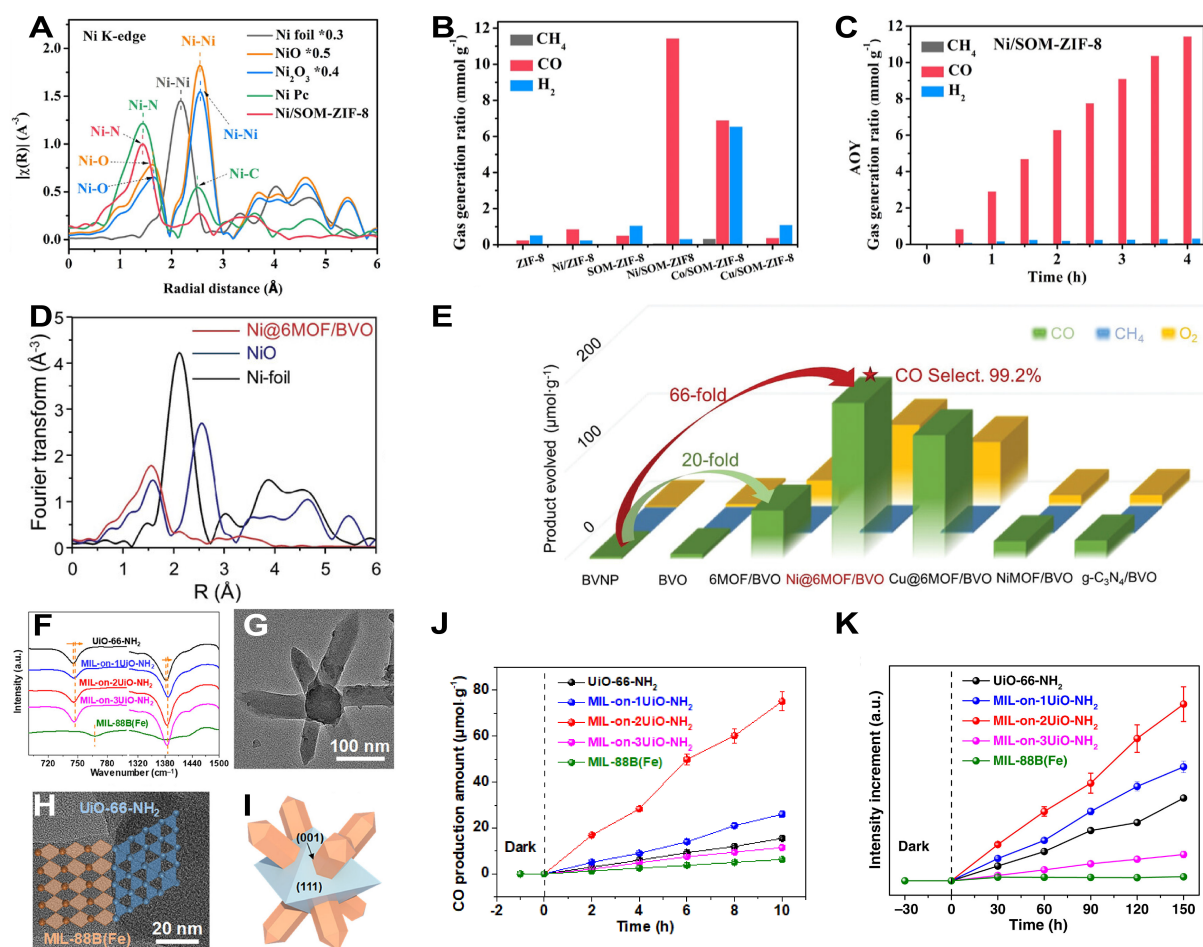


Figure 17. (A) FT-EXAFS spectra of the Ni K-edge for Ni/SOM-ZIF-8 and other catalysts; (B) Photocatalytic CO_2RR performance of 6 different ZIF-8 based catalysts; (C) Cumulative production of CO , CH_4 and H_2 by Ni/SOM-ZIF-8; (A-C) are quoted with permission from Liu *et al.* [274]; (D) FT-EXAFS spectra of the Ni K-edge for Ni@6MOFs/BVO; (E) Photoactivities of CO_2RR over Ni@6MOFs/BVO and other reference samples; (D and E) are quoted with permission from Zhao *et al.* [275]; (F) ATR-FTIR spectra of MIL-on-2UiO-NH₂ and other reference samples; (G-I) TEM image (G), HRTEM image (H), and Schematic diagram (I) of MIL-on-2UiO-NH₂; (J) Production of CO over MIL-on-2UiO-NH₂ and other reference samples; (K) Detection of $\cdot\text{OH}$ radical trapping efficiency with 7-hydroxycoumarin at 457 nm over MIL-on-2UiO-NH₂ and other reference samples by PL spectrometer; (F-K) are quoted with permission from Li *et al.* [276]. SOM: Surfactant-assisted ordered mesoporous; ZIF: zeolitic imidazolate framework; MOF: metal-organic framework; BVO: BiVO_4 ; BVNP: bismuth vanadate nanoparticles; MIL: materials of Institut Lavoisier; FT: Fourier transform; EXAFS: extended X-ray absorption fine structure; CO_2RR : CO_2 reduction reaction; TEM: transmission electron microscope.

selectivity for CO [Figure 17B]. The cumulative production yield of Ni/SOM-ZIF-8 indicated a progressive rise in CO yield while unchanging for H_2 , demonstrating good stability [Figure 17C]. Zhao *et al.* synthesized NTU-9 (bulky MOFs) via solvothermal methods and subsequently coupled Ni@MOFs with BiVO_4 (BVO) nanosheets through induced assembly to obtain a single atomic Ni@MOFs/BVO heterojunction catalyst for photocatalysis [275]. FT-EXAFS spectra of the Ni K-edge for Ni@MOFs/BVO showed that no peaks of Ni–Ni bond in Ni@MOFs/BVO were found at 2.15 $\text{\AA}$ [Figure 17D]. The photocatalytic CO_2 reduction activities of various materials were compared [Figure 17E]. The prepared Ni@MOFs/BVO exhibited the best catalytic property, with a CO generation of $178 \mu\text{mol g}^{-1}$ and a CO selectivity of 99.2%, representing a 66-fold increase in CO_2 photoconversion efficiency compared to BVO nanoparticles, while effectively suppressing H_2 production and nearly 100% CO selectivity. Li *et al.* synthesized materials such as UiO-66-NH₂, MIL-88B (Fe), and MIL-on- x UiO-NH₂ ($x = 1, 2, 3$) via solvothermal reactions [276]. The Attenuated total

reflectance-Fourier transform infrared (ATR-FTIR) spectrum indicated a blue shift of the Zr-oxo cluster and carboxylate stretching bands, suggesting coordination between the Zr-oxo clusters of UiO-66-NH₂ and the benzene rings of MIL-88B (Fe), establishing a chemical link between the two [Figure 17F]. The HRTEM image, TEM images and structural schematics revealed that MIL-on-2UiO-NH₂ exhibited a specific rod-octahedral structure, formed through an epitaxial growth method [Figure 17G-I]. In the photocatalytic CO₂ reaction using triethanolamine as a sacrificial agent, MIL-on-2UiO-NH₂ maintained high CO generation activity, with CO selectivity approaching 100% [Figure 17J]. Specifically, without employing a sacrificial agent, the CO generation rate of MIL-on-2UiO-NH₂ was approximately 2.26 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. In the photocatalytic process for capturing OH radicals to form 7-hydroxycoumarin, photogenerated holes accumulated on the UiO-66-NH₂ side [Figure 17K].

In addition to the single product reduction (CO) mentioned above, MOFs-based SACs could also be used for multi-product reduction in photocatalytic CO₂RR^[277]. Pan *et al.* prepared CA/Ni₁Cu_{NP} N-C using an ion exchange strategy followed by calcination^[278]. Based on the EXAFS fitting results, it was found that Ni atoms in CA/Ni₁Cu_{NP} N-C predominantly existed in a form coordinated with four N atoms, with a coordination number determined to be approximately 3.6 and a bond length of about 1.86 Å [Figure 18A]. Photocatalytic experiments showed that with the increasing proportion of CA/Ni₁Cu_{NP} N-C in the composite material, the yields of CH₄, CO, and C₂H₆ exhibited a trend of first increasing and then decreasing, achieving optimal catalytic performance at CA/Ni₁Cu_{NP} N-C (1:2) [Figure 18B]. The transfer of electrons generated by light from CoAl-LDH to N-C ultimately accumulated at dispersed single atom sites of Ni to drive the reaction [Figure 18C]. Zeng *et al.* employed an *in situ* synthesis method by immersing Mil-125 in CoPy₄ solution followed by calcination to prepare CoN_x cluster-modified TiO₂ (CoN_x/TiO₂) catalysts^[279]. The AC-HADDF-STEM image of CoN_x/TiO₂ indicated a uniform dispersion of CoN_x clusters in TiO₂, where the bright contrast spots represented the positions of Co atoms within the TiO₂ lattice [Figure 18D]. Under irradiation with a 300 W Xe lamp, the photocatalytic activity of CoN_x/TiO₂ varied with the amount of CoPy₄ added, with CoN_x/TiO₂-4.0 achieving the highest CO/CH₄ yield (24.4/119.9 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$) and top photocatalytic activity (1,007.6 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$), which were 10.6 times and 4.6 times that of TiO₂ and CoO_x/TiO₂, respectively [Figure 18E and F]. Wang *et al.* synthesized Cu isolated-atom modified UiO-66-NH₂ catalyst (Cu SAs/UiO-66-NH₂) using a photoinduction method^[280]. The XANES spectrum indicated that the absorption edge of Cu SAs/UiO-66-NH₂ was positioned between the edges observed for Cu and CuO [Figure 18G]. In presence of Cu SAs/UiO-66-NH₂, the liquid-phase products of photocatalytic CO₂ reduction were detected to be only CH₃OH and CH₃CH₂OH, indicating that this catalyst was selective for these two liquid fuels [Figure 18H]. The rate of CH₃OH production by Cu SAs/UiO-66-NH₂ was approximately 5.33 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ while that of CH₃CH₂OH was 4.22 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, significantly far more than those of other samples, demonstrating that the addition of isolated Cu atoms obviously boosted the catalytic efficiency [Figure 18I].

For MOFs-based DACs in photocatalytic CO₂RR, Yuan *et al.* prepared one Cu-In double atomic MOFs-based catalyst (CuIn-DACs) through pyrolysis and etching^[281]. As shown in EDS-mapping images of CuIn-DACs, Cu, In, C, and N were homogeneously dispersed in the CuIn-DACs [Figure 19A]. The Cu-In double atoms were distributed within CuIn-DACs at atomic level [Figure 19B], fully exerting the collaborative catalytic action of dual atoms. The FE for methanol of CuIn-DACs reached 55.63% at -0.62 V vs. RHE, significantly far more Cu-SACs, indicating a higher selectivity for methanol and effectively promoting the conversion of CO₂ to methanol while suppressing other side reactions [Figure 19C]. Tan *et al.* synthesized MnS/In₂S₃ p-n heterojunctions using MIL-68 (In) sub-microrods as templates followed by impregnation and sulfidation^[282]. In photocatalytic CO₂RR, 30 wt.% MnS/In₂S₃ showed optimal CO generation rate, reaching 58 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, while the CO generation rates for In₂S₃ and MnS were only about 14 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and 16 $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$, respectively [Figure 19D]. This indicated that the formation of the MnS/In₂S₃ significantly

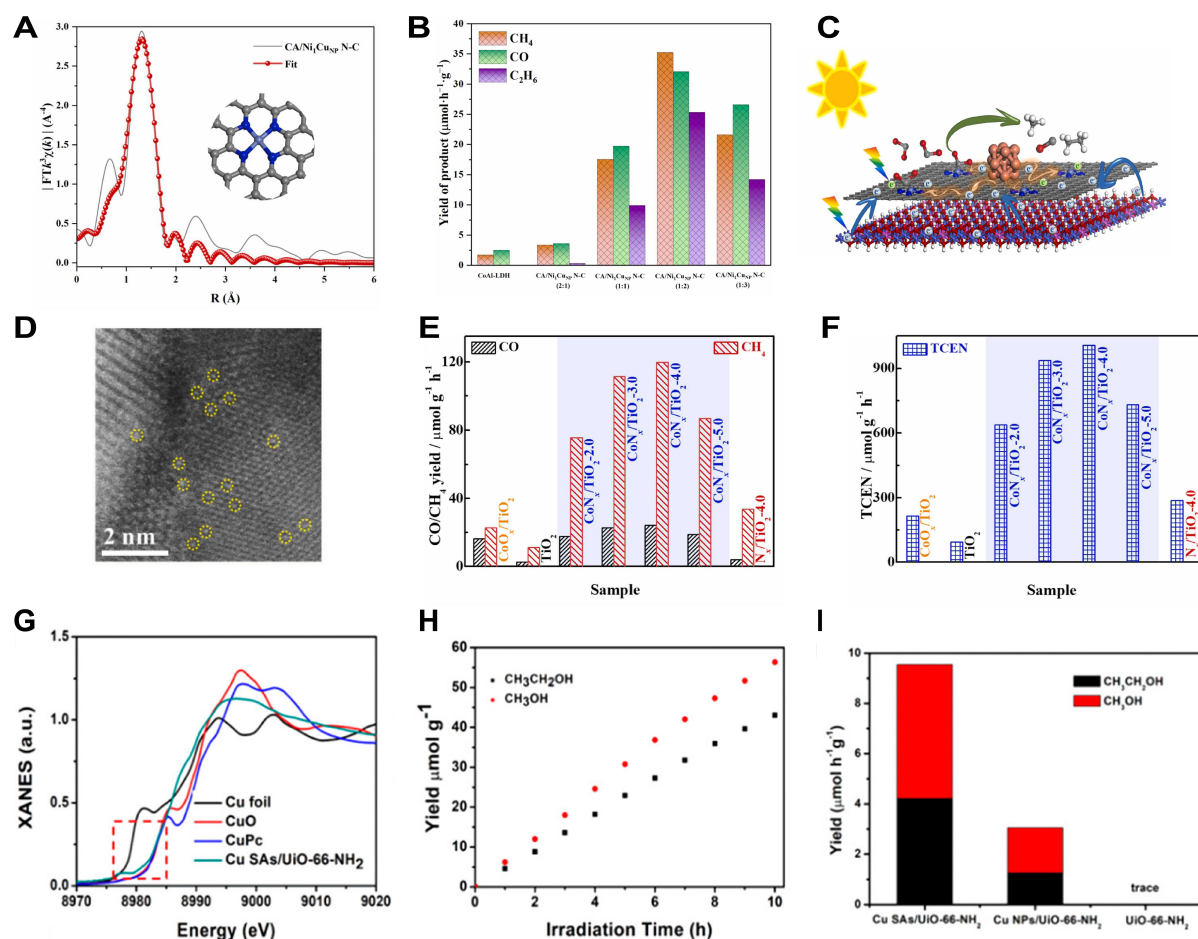


Figure 18. (A) FT-EXAFS fitting and structural model of CA/Ni₁CuNP N-C; (B) Photocatalytic CO₂RR product efficiency of CH₄, CO, and C₂H₆ with different percentage of Ni₁CuNP N-C; (C) Diagram of photocatalytic CO₂RR mechanism over Ni₁CuNP N-C; (A-C) are quoted with permission from Pan *et al.* [278]; (D) AC-HAADF-STEM image of Co_xN_x/TiO₂; (E and F) CO/CH₄ yields (E) and the corresponding TCEN (F) of Co_xN_x/TiO₂ and other reference samples; (D-F) are quoted with permission from Zeng *et al.* [279]; (G) Normalized XANES spectra of the Cu K-edge for Cu SAs/UiO-66-NH₂ and other samples; (H and I) CH₃OH/CH₃CH₂OH yields (H) and comparative rates of formation (I) by Cu SAs/UiO-66-NH₂; (G-I) are quoted with permission from Wang *et al.* [280]. FT: Fourier transform; EXAFS: extended X-ray absorption fine structure; CO₂RR: CO₂ reduction reaction; XANES: X-ray absorption near-edge structure; TCEN: total carbon-based product.

enhanced photocatalytic activity. After the formation of the heterojunction between In₂S₃ and MnS, the photocurrent density was significantly increased [Figure 19E]. The p-n heterojunction effectively promoted charge separation and improved the utilization efficiency of photogenerated carriers. After a 10-hour photocatalytic CO₂ reduction experiment with the 30 wt.% MnS/In₂S₃ catalyst, XRD analyses showed no significant changes in structure, indicating structural stability under photocatalytic conditions [Figure 19F]. Hu *et al.* prepared CuNi SAs/UiO-66(Hf) using one combined method of hydrothermal fixation and radiation reduction [283]. In a saturated aqueous solution of CO₂ irradiated with ⁶⁰Co γ-rays, the blank experiment yielded no carbonaceous products. UiO-66(Hf) caused a slight increase in CO production, while CuNi SAs/UiO-66(Hf) could generate CH₃OH but with poor selectivity. The addition of Na₂SO₃ allowed a small amount of CuNi SAs/UiO-66(Hf) to achieve a CH₃OH selectivity of 97.8%, significantly enhancing the G value [Figure 19G]. As the CuNi SAs/UiO-66(Hf) weight ratio increased from 0.05% to 0.2%, the G value increased from $0.9 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$ to $1.5 \times 10^{-7} \text{ mol} \cdot \text{J}^{-1}$, indicating that enhancing the weight ratio of catalyst could effectively promote CH₃OH generation [Figure 19H].

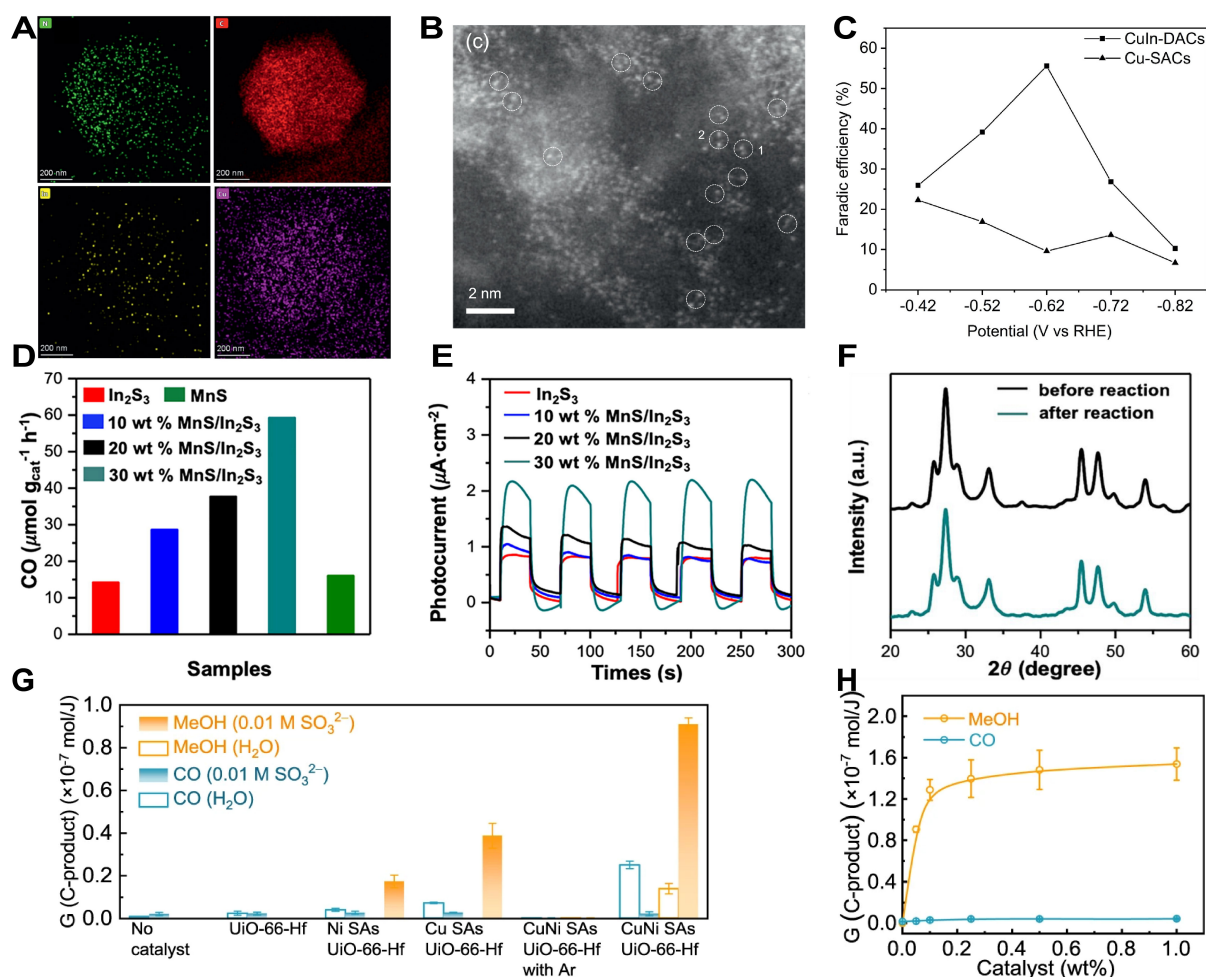


Figure 19. (A and B) EDS-mapping images (A) and HAADF-STEM image (B) of CuIn-DACs; (C) FE_{methanol} of CuIn-DACs and Cu-SACs; (A-C) are quoted with permission from Yuan et al.^[281]; (D) CO product rate of different catalysts; (E) Transient photocurrents of different catalysts; (F) XRD patterns of MnS/In₂S₃ catalyst before and after photocatalytic CO₂RR experiment (10 h); (D-F) are quoted with permission from Tan et al.^[282]; (G) G-value_{MeOH} and G-value_{CO} of 0.05 wt.% with CuNi SAs/UiO-66(Hf) and other catalysts in H₂O or 0.01 M Na₂SO₃ solution; (H) The amplified G-value_{MeOH} and G-value_{CO} by the increase of CuNi SAs/UiO-66(Hf) content; (G and H) are quoted with permission from Hu et al.^[283]. RHE: Reversible hydrogen electrode; EDS: energy-dispersive X-ray spectroscopy; HRTEM: high-resolution transmission electron microscopy; DACs: dual-atom catalysts; SACs: single-atom catalysts; XRD: X-ray diffraction; CO₂RR: CO₂ reduction reaction.

CONCLUSION AND OUTLOOK

Attributable to the excellent activity of active sites in SACs and DACs, combined with the superior mass transfer and photoelectric performance of MOFs, MOFs-based SACs/DACs could be used as an ideal bridge connecting heterogeneous catalysis and homogeneous catalysis, with high selectivity and high activity, as well as strong durability, and excellent performance in electrocatalytic and photocatalytic CO₂RR. This review systematically introduces the design and regulation of MOFs-based SACs/DACs active sites together with the characterization of active sites. Moreover, the mechanism of electrocatalytic and photocatalytic CO₂RR is analyzed carefully, especially emphasizing the relationship between the active sites and catalytic efficiency. Finally, recent processes of MOFs-based SACs/DACs in electrocatalytic and photocatalytic CO₂RR are summarized.

Although the significant progress of MOFs-based SACs/DACs in electrocatalytic and photocatalytic CO₂RR has been achieved, the challenges of the future directions for active sites design and the development of improving catalytic activity in CO₂RR at industrial current density of MOFs-based SACs/DACs still exist and need to be addressed in future studies.

(1) The coordination conditions of the active sites seriously influence the activity of MOFs-based SACs/DACs; however, the basis of the formation of different coordination environments is not clear, especially the physical basis. Although in many previous works, different active sites were prepared by changing the pyrolysis temperature or the ratio of coordination atoms to feed, these methods were still in the experimental stage of small-scale production, and did not form a regular and certain scale. Furthermore, the limited number of active sites in MOFs restricts the provision of high-density metal sites. Therefore, the mechanism of active site formation and the mature method of large-scale production of high-density MOFs-based SACs/DACs need to be explored further. For example, in the preparation process of MOFs-based SACs/DACs, the structure of the intermediate product is qualitatively or quantitatively analyzed, and the formation process of the active site is gradually explored.

(2) From various studies and analyses, it could be seen that MOFs-based SACs/DACs with many advantages are superior to other catalysts, especially the synergistic impact of the active sites of polymetallic atoms, which could not be compared with a single metal atom. For MOFs-based SACs/DACs over CO₂RR, the reduction products are also diverse; there is a single product CO, which could also be complex products, such as CO and methane. These are all C₁ products. There are very few studies on the C₂ products of MOFs-based SACs/DACs in CO₂RR, because the generation of C₂ products requires higher requirements on the active site, which requires the generation of C–C bonding. Therefore, the research progress of MOFs-based SACs/DACs in multi-carbon products of CO₂RR needs to be further explored.

(3) Many catalysts lack selectivity for CO₂ in CO₂RR. For MOFs-based SACs/DACs, selectivity and activation of CO₂ could be improved by selecting characteristic high metal active sites and regulating and optimizing the coordination environment between active sites and organic ligands. The catalyst activity could be improved by adding metal nanoparticles or clusters, adjusting the valence state of the metal center to achieve low coordination, and selecting organic ligands with oxygen bridge structure. Furthermore, the selectivity of CO₂ in MOF-based SACs/DACs can also be enhanced by modifying the MOF structure. This includes constructing core-shell or multi-layer nanosheet architectures using the MOFs-on-MOFs approach.

(4) In the evaluation of various performances of MOFs-based SACs/DACs, stability is an essential item. Although through various characterization methods, we could observe that the active sites are distributed in atomic states of MOFs-based SACs/DACs, this is only the preparation conditions in the laboratory. Industrial catalysis demands that catalysts exhibit long-term stability and reliability, alongside high activity. For large-scale industrial production, especially under high-temperature conditions and special reducing atmospheres, the active sites in MOFs-based SACs/DACs are very likely to be lost, aggregated or redistributed. Therefore, first, under laboratory conditions, we need to ensure that the synthesized MOFs-based SACs/DACs have long-term thermodynamic stability through a series of explorations at different times, while maintaining a high activity state. By modifying the coordination number of central metallic atoms in MOFs-based SACs/DACs, too low coordination could indeed bring about high activity, but it could seriously affect stability. Therefore, balancing the stability and activity of the MOFs-based SACs/DACs is an important challenge. In addition, for large-scale production of catalysts, from the perspective of the environmental cost of preparation, we still have to follow the principle of green chemical preparation.

DECLARATIONS

Authors' contributions

Writing-original draft: Li, J.; Zhang, W.

Investigation: Peng, Y.; Wu, Q.; Zhu, W.

Data curation, validation: Zhang, Y.; Wang, S.

Conceptualization, methodology, resources: Liu, S.; Wang, D.; Dai, Z.

Availability of data and materials

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Conflicts of interest

All authors declared that there are no conflicts of interest.

Ethical approval and consent to participate

Not applicable.

Consent for publication

Not applicable.

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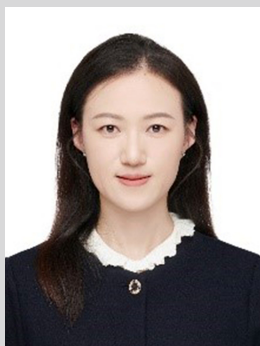
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