



Design of efficient dual-atom catalysts for energy conversion

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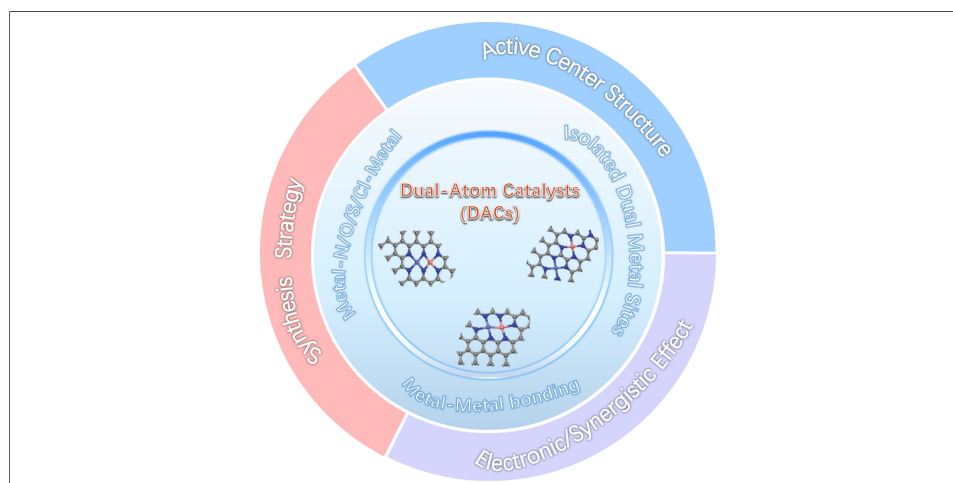
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Abstract

Dual-atom catalysts (DACs) have triggered the burgeoning interest in the field of catalysis. The identification of coordination structures and the understanding of the catalytic role of dual-atom centers are of great significance to designing highly efficient DACs. This review summarizes the current synthesis methods for the construction of DACs. Then, we highlight the differences in geometric and electronic structures of DACs in terms of modulation strategies and engineering dual-metal interaction. In particular, the combination of various advanced characterizations and density functional theory (DFT) insights disclose the state of the dual-atom active center microenvironment. Moreover, the catalytic role of DACs in heterogeneous catalysis is discussed, involving the electronic effect of one metal as the main active center and the synergistic effect between dual metals. The structure-activity relationship and reaction mechanism based on experimental studies and theoretical exploration are discussed. Finally, the challenges and opportunities of DACs for the efficient valorization of energy-related small molecules are proposed. This review can offer new inspiration on developing DACs for energy conversion.



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INTRODUCTION

With the growing energy crisis and global population caused by the excessive consumption of fossil fuels, significant efforts have been devoted to developing clean energy conversion technologies^[1-3]. Most of them are related to the catalytic processes, particularly electrocatalysis showing a promising platform to reduce fossil fuel dependence^[4-7]. Designing effective catalysts with remarkable reactivity is important for catalytic reactions and industrial applications. Taking advantage of robust and easy separation, heterogeneous catalysts especially supported metal catalysts are widely investigated^[8-12]. To improve the performance, a simple method is to decrease the particle size of metals to the nanoscale. In this regard, the finding that Au nanoparticles are active for carbon monoxide oxidation at cryogenic temperatures has ignited excitement in nanocatalysis^[13]. The ultimate goal is to achieve single-atom dispersion of metal species.

Single-atom catalysts (SACs) have been a new frontier in catalysis during the past decade, which have been widely investigated owing to their high atom utilization and distinct structure^[14-23]. In 2011, Qiao *et al.* proposed the concept of “single-atom catalysis” for the first time^[24]. The intrinsic activity of SACs can be enhanced by further tailoring the electronic state and coordination structure^[25-29]. Despite achieving significant progress, the challenges still lie in the development of SACs. To keep the single-atom dispersion, the metal loading of SACs is usually low (< 1.5 wt%) to avoid aggregation; thus, the total activity is not satisfactory^[30-35]. In addition, since the active center of SACs is single, it is difficult to break the limitation by a linear scaling relationship. Moreover, SACs may not be desired for reactions that need different metal sites to activate reactants or multiple-step catalytic processes.

Dual-atom catalysts (DACs), as an extension of SACs, have attracted much attention in recent years^[36-40]. The timeline of the representative breakthroughs in DACs is presented in Figure 1^[24,41-47]. The addition of the other metal atoms into SACs can improve the metal loadings, tune the electronic structures, and break the linear relationship. Generally speaking, the d-band center will be adjusted owing to the coordination of the adjacent two atoms. Furthermore, DACs provide more active sites to adsorb and activate the reactants, giving priority to realizing multiple reaction pathways^[48-54]. Benefiting from the synergistic effect, DACs are promising candidates for catalyzing tandem reactions via rational design. At present, several reviews on preparation, characterization, and electrochemical application have been reported^[55-60]. However, these papers mainly focus on homonuclear and heteronuclear DACs and relevant applications in electrocatalysis. So far, identifying the active structure and understanding the catalytic role of DACs in heterogeneous catalysis are still lacking.

In this review, we first present an overview of synthetic approaches for DACs, involving atomic layer deposition (ALD), wet chemical approach, high-temperature pyrolysis, and atom trapping. We introduce and discuss the different principles to guide the dual-atom design on diverse substrates. Next, we highlight the identification of active center structures of DACs, with a focus on elucidating local environments and dual-atom interactions. Moreover, we illustrate the catalytic role of DACs in boosting performance and disclose the reaction mechanisms, involving electronic effect and synergistic effect. Finally, the current challenges and future opportunities of DACs are put forward to point out directions for the development of DACs.

SYNTHESIS STRATEGIES OF DACs

The fabrication of DACs is more rigorous than that of SACs due to diverse requirements. Developing facile preparation methods becomes an important issue to be solved. First, the interaction between metal precursors and substrates is critical to stabilize the metal dimers. Another feasible approach is via spatial confinement utilizing porous materials, such as metal-organic frameworks (MOFs) and covalent organic

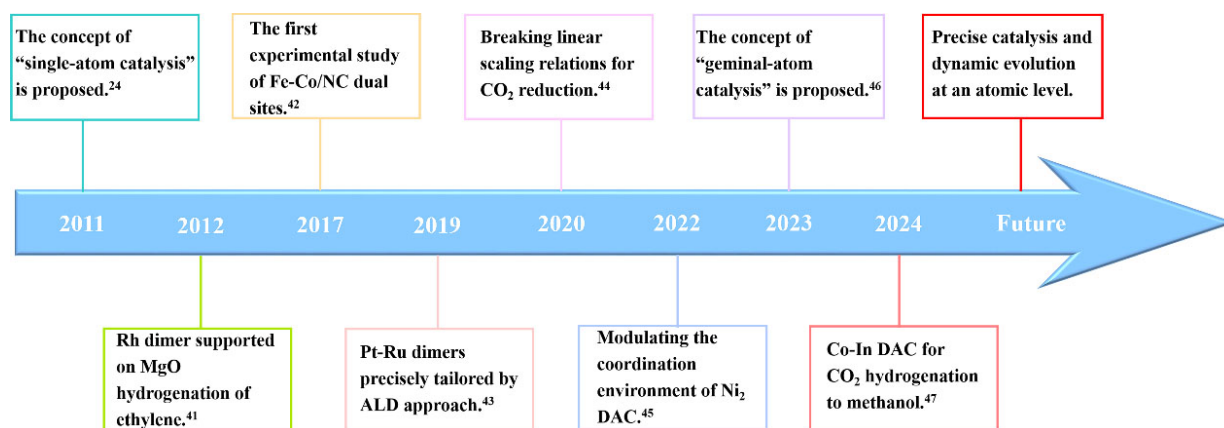


Figure 1. Timeline of breakthroughs during the last decade of DACs. DACs: Dual-atom catalysts; ALD: atomic layer deposition.

frameworks (COFs). In this part, we summarize the preparation methods of DACs, including ALD, wet chemical approach, high-temperature pyrolysis, and atom trapping. It is worth mentioning that the synthetic approaches reported up to now are still in their infancy, with expensive reagents and high-temperature conditions. The effective and controllable synthesis needs to be explored in the future.

Atomic-layer deposition

The ALD method is a powerful tool for the precise control of catalysts from clusters to single atoms. The ALD process involves two sequential self-limiting surface reactions separated by inert gas sweeping^[61,62]. This unique character makes the ALD technique possible to construct single or few atoms on high-surface-area support controllably and precisely. Besides, dimers prepared by ALD may be different from the reported dual-metal sites. As a typical example, Pt-Ru dimers on nitrogen (N)-doped carbon nanotubes (NCNT) were synthesized by the ALD process^[43]. As shown in [Figure 2A](#), the single Pt atoms were obtained by using MeCpPtMe₃ as the precursor and nitrogen as the purge gas. The Pt atoms tend to bond with N sites on NCNT by forming strong interactions. Then, Ru atoms were selectively dispersed on Pt atoms to form Pt-Ru dimers. The atomic resolution electron microscopy images showed dimers dispersed on the substrate [[Figure 2B](#)]. The two atoms exhibited distinct contrasts, indicating that the dimer structure contained two different elements, Pt and Ru [[Figure 2C](#)]. The detailed characterization and theoretical calculation indicated that the electronic state of Ru was strongly affected by the Pt atom, resulting in good hydrogen evolution activity. In the synthesis of Pt₂ dimers, nucleation sites were firstly constructed on graphene nanosheets via acid oxidation followed by thermal reaction^[63]. The Pt₁ single atoms were first generated by alternately exposing MeCpPtMe₃ and O₂. Then, these atoms were further used as nucleation sites for binding the second MeCpPtMe₃ to form Pt₂ dimers. Furthermore, to regulate the interspace of Pt₁ and Ni₁ atoms, Chen *et al.*^[64] fabricated Pt₁Ni₁ oxo dimers and Pt₁+Ni₁/C₃N₄ DAC by ALD [[Figure 2D](#)]. The aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC HAADF-STEM) showed single Ni₁ and Pt₁ in relatively dark and bright contrasts dispersed on C₃N₄ [[Figure 2E](#)]. The average Pt-Ni distance was 2.2 Å in the dimeric Pt₁Ni₁ structure, while the distance between Ni₁ and Pt₁ atoms was about 4.9 Å in the Pt₁+Ni₁/C₃N₄ sample. In addition, the valence analysis revealed that the Pt₁ atom in Pt₁Ni₁ was more positively charged than those in the Pt₁ + Ni₁ sample, indicating electron transferring from Pt₁ to Ni₁. This work demonstrates the key role of atom-atom interspace in synergetic catalysis.

Wet chemical method

The wet chemical method is the most intensively used approach for synthesizing supported metal catalysts. It has been illustrated as an effective strategy to construct well-dispersed atomic pairs on substrates with suitable anchoring sites. Li *et al.* prepared an Ag₂/graphene catalyst with an AgN₃-AgN₃ site via the wet

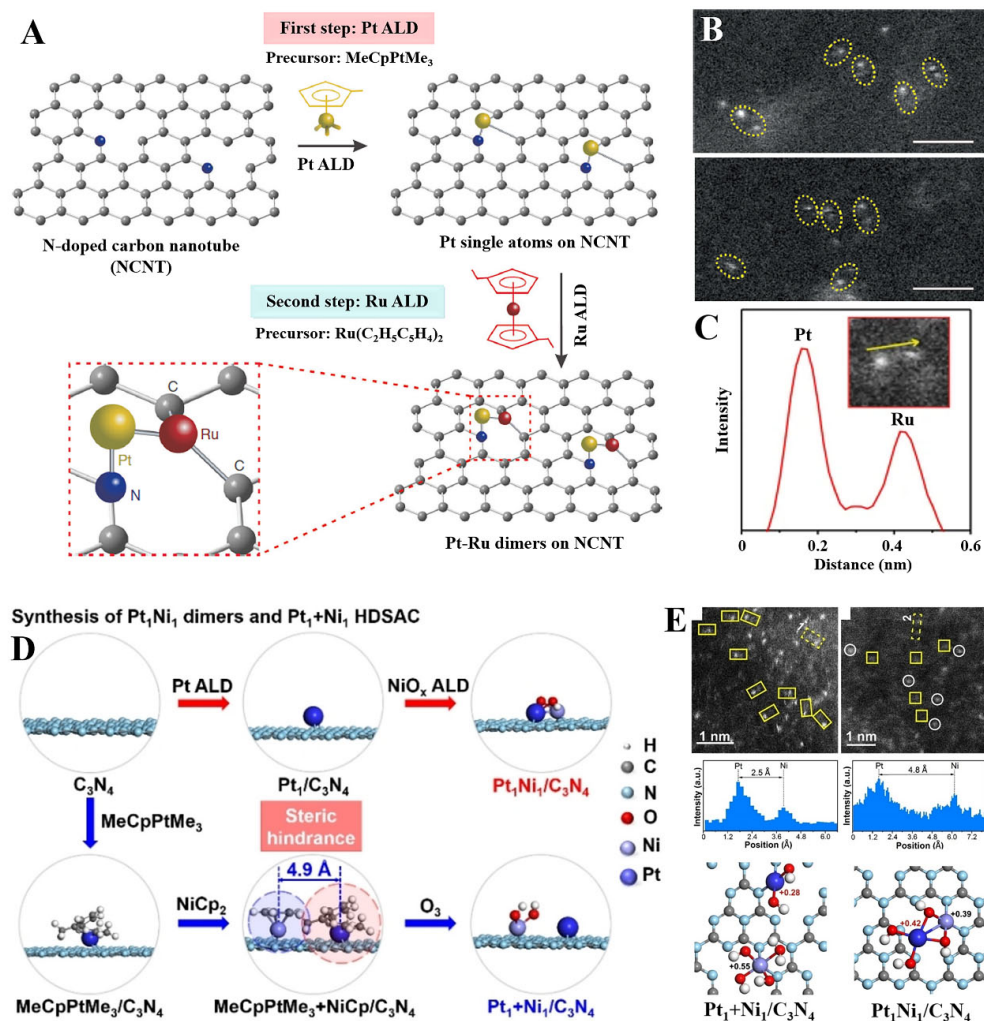


Figure 2. (A–C) The preparation of DACs by ALD and AC HAADF-STEM images of Pt–Ru pairs. Reproduced with permission from Ref.^[43]. Copyright 2019, Nature Publishing Group; (D) The schematic synthesis of Pt₁Ni₁/C₃N₄ and Pt₁+Ni₁/C₃N₄ dimers; (E) AC HAADF-STEM images and structural models; (D–E) Reproduced with permission from Ref.^[64]. Copyright 2022, Wiley-VCH. DACs: Dual-atom catalysts; ALD: atomic layer deposition; AC HAADF-STEM: aberration-corrected high-angle annular dark-field scanning transmission electron microscopy.

chemical method^[65]. Typically, the binuclear Ag complex containing aromatic molecules was prepared and used as the metal precursor. Then, the precursor was adsorbed on the graphene surface via π - π interaction, and the ligands were removed by following the pyrolysis process. Besides, Cu₂ dimers anchored on carbon nitride were fabricated for efficient partial oxidation of methane^[66]. Similarly, the Cu dimer precursor was first synthesized by complexation reaction, followed by self-assembly of Cu dimer complex on g-C₃N₄. Subsequently, the mixture was treated at 250 °C in air to anchor Cu species via Cu–N bonding. As shown in Figure 3A, the Ni₂ site comprising two N atoms bridged Ni–N₄ structures was prepared toward electrocatalytic CO₂ reduction^[67]. The ligand-protected dinuclear Ni₂(dppm)₂Cl₃ precursor was first prepared by a controllable sluggish reaction of NiCl₂ and dppm complex. The precursor was then impregnated with zeolite imidazolate framework 8 (ZIF-8)-derived carbon. Finally, the mixture was pyrolyzed at 400 °C in Ar to remove the organic ligands, resulting in the formation of a diatomic Ni₂/N-doped carbon (NC) catalyst. The corresponding AC HAADF-STEM image demonstrated Ni₂ species uniformly dispersed on the NC substrate [Figure 3A]. Interestingly, it was found that the coordinated unsaturated Ni could adsorb oxygen species in the electrolyte, producing an O–Ni₂–N₆ configuration, which decreased the energy barrier for the

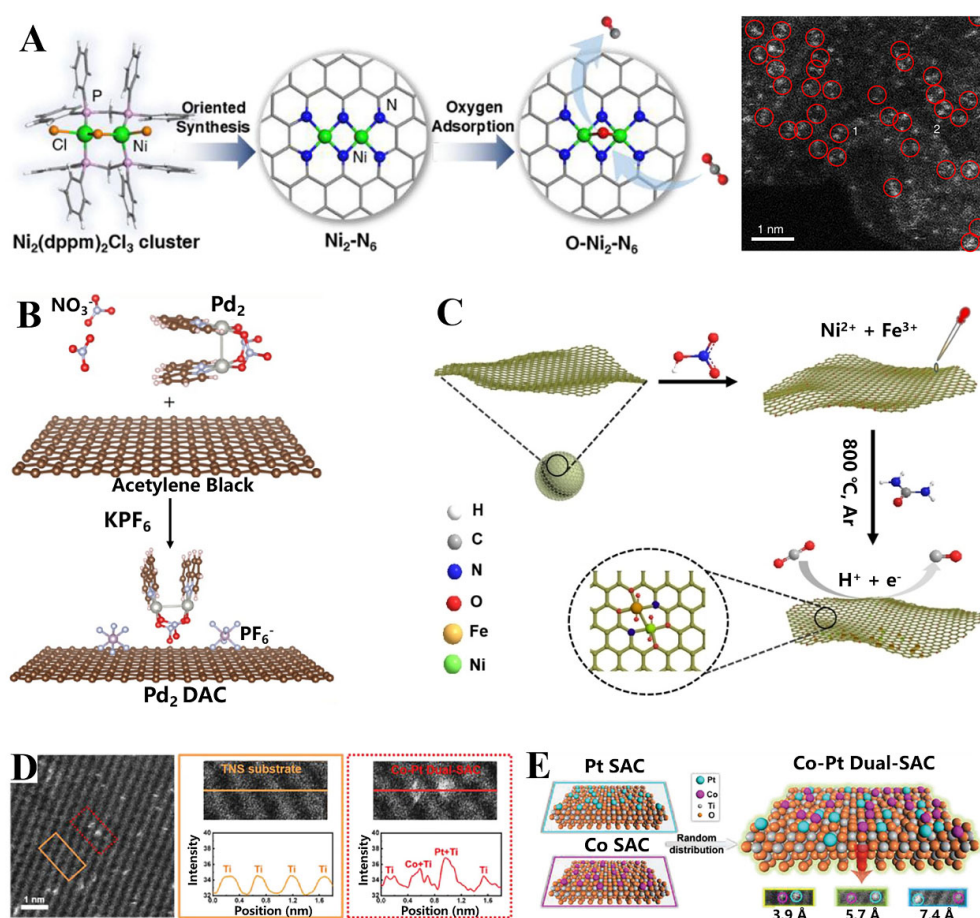


Figure 3. (A) The preparation strategy for dinuclear Ni₂/NC and atomically dispersed Ni₂ species highlighted by red circles. Reproduced with permission from Ref.^[67]. Copyright 2021, American Chemical Society; (B) The synthesis strategy for Pd₂ DAC. Reproduced with permission from Ref.^[70]. Copyright 2021, Wiley-VCH; (C) Schematic of synthesis of dual-atom Ni/Fe on carbon blacks. Reproduced with permission from Ref.^[73]. Copyright 2021, Wiley-VCH; (D) Atomic scale identified the brightness of Pt and Co dual atoms in the selected area; (E) Schematically illustration of random atomic sites; (D-E) Reproduced with permission from Ref.^[75]. Copyright 2021, Wiley-VCH. DACs: Dual-atom catalysts; SACs: single-atom catalysts.

activation of CO₂ and enhanced CO₂ reduction to CO performance. Using a dinuclear Ni complex as the precursor, dual-atom Ni₂ supported on NCNT was developed^[68]. It was indicated that the directly bonded NiN₃-NiN₃ structure decreased the reaction energy for *COOH generation and promoted CO₂ electroreduction. By changing the type of metal precursors, Tian *et al.* prepared diatomic Fe₂ dispersed mesoporous carbon nitride, which exhibited superior activity toward alkene epoxidation^[69]. Furthermore, they anchored the dinuclear Pd₂ precursor on acetylene black as displayed in Figure 3B, and KPF₆ was added to ensure the Pd deposited on the surface of the carbon substrate^[70]. Yu *et al.* synthesized dinuclear Ir₂ sites bridged by oxygen on NC, which exhibited higher activity than Ir SACs for electrochemical chlorine evolution reaction^[71]. In particular, Guan and Yardimci *et al.* chose MgO as the substrate to stabilize Ir or Rh pairs due to its basic surface sites that facilitated the precise synthesis of well-defined supported species^[41,72]. These advances demonstrate that the wet-chemistry route is a feasible strategy for the controlled preparation of DACs by tuning the ligands or metal centers of precursors.

Apart from homonuclear dual atoms, the precursor-preselected wet-chemistry strategy is also effective for the construction of heteronuclear dual atoms. As presented in Figure 3C, the Ni/Fe-NC dimers were prepared by a two-step procedure^[73]. In brief, carbon black was activated by nitric acid to trap and adsorb

Ni²⁺ and Fe²⁺ atoms. Subsequently, the Ni and Fe atoms were supported on the carbon substrate by pyrolysis and acid leaching process. Interestingly, the Ni/Fe-NC diatomic catalyst exhibited outstanding activity and turnover frequencies ($\sim 460\text{ s}^{-1}$) for electroreduction of CO₂ to CO. Additionally, a N/P coordinated Fe-Co DAC was designed on a ZIF-8-derived carbon substrate^[74]. To guarantee the uniform composition of Fe-Co dual atoms, the molecule of C₃₄H₂₈Cl₂CoFeP₂ confining a pair of Fe/Co ions and P ions was selected as an ideal precursor. After pyrolyzing in Ar, the FeCoN₅P₁ catalyst was obtained. By comparing with N coordination (FeCoN₆), the introduction of P coordination (FeCoN₅P₁) significantly improved stability in fuel cells. Other than carbon supports, metal oxides are ideal hosts to stabilize dual-metal atoms. In this case, Wang *et al.* prepared Co and Pt dimers, consisting of Co-O-Pt pairs on TiO₂ nanosheets^[75]. As presented in Figure 3D, the Co and Pt single atoms were observed as the bright spots. The intensity of these bright spots was further quantified, confirming the Co and Pt atoms. The dual-atom configuration was schematically presented in Figure 3E where Co and Pt dual atoms were anchored simultaneously and randomly on TiO₂(101) facets. It was demonstrated that the Co-O-Pt dimer achieved an outstanding photocatalytic hydrogen evolution performance. However, the number fraction of dimer sites in this catalyst is only 13.4%. Future opportunities exist on further increasing the fraction of Co-O-Pt pairs to improve the catalytic efficiency.

The above advances suggest several critical factors for the controlled preparation of dual atoms by the wet chemical method: (1) selecting appropriate binuclear metal complexes and moderate interaction with substrates. Particularly, a strong interaction between binuclear metal and the substrate is significant for obtaining high dispersion and stable DACs; (2) constructing porous substrate to take full advantage of the pore confinement effect to stabilize diatomic metals; (3) taking advantage of functional groups or defects on the surface of substrates to stabilize metal complexes; (4) using the π - π electrostatic interplay to anchor binuclear metal complexes. The corresponding approaches have been verified to be effective in obtaining highly dispersed DACs.

High-temperature pyrolysis

The high-temperature pyrolysis is a commonly used method for fabricating SACs and DACs, especially in NC-supported metal catalyst systems. MOFs are extensively considered as the precursors for pyrolysis. On the one hand, MOFs can be facilely tuned by regulation of metal nodes or organic linkers with some functions^[76]. On the other hand, they possess abundant pores that confine different metal species, making them a promising candidate to stabilize single and few atoms^[77,78]. In recent work, Lu *et al.* reported a competitive complexation strategy to synthesize isolated Zn-Co atomic pairs^[79]. As presented in Figure 4A, chitosan was chosen as C and N sources, and zinc chloride and cobalt acetate were used as metal precursors. The 4s and 4p electrons of Co²⁺ and Zn²⁺ could be bound with the -NH₂ and -OH on chitosan chains, thus obtaining the uniform dispersion of Co and Zn atoms after pyrolysis at 750 °C. The characterization and DFT calculations revealed ZnCoN₆ as an active site; such architecture enhanced the activation ability of O₂, thus leading to outstanding oxygen reduction performance. In another work, the monomer melamine, L-aspartic acid, and salts of Co and Ni were mixed and polymerized under hydrochloric acid initiation. The N-doped graphene anchored N₃-Co-N-Ni-N₃ site was synthesized after pyrolysis at 800 °C^[80]. The N-bridged Ni and Co dual atoms (Co-N-Ni) achieved high performance for polystyrene degradation. The above approaches involve two steps: first, the precursor of metal salts is coordinated with ligands, followed by pyrolysis under an inert atmosphere to produce dual atoms.

In addition, the preparation of DACs via pyrolysis of MOF precursors is an epidemic method. Wang *et al.* designed Fe-Co atomic pairs based on control over binding between Co nodes and adsorbed Fe within the confined space of MOFs^[42]. The Fe-Co/NC comprising Fe-Co direct bonding structure was formed after heating at 900 °C. Benefiting from the MOF-assisted host-guest strategy, isolated Ni/Co dual atoms anchored

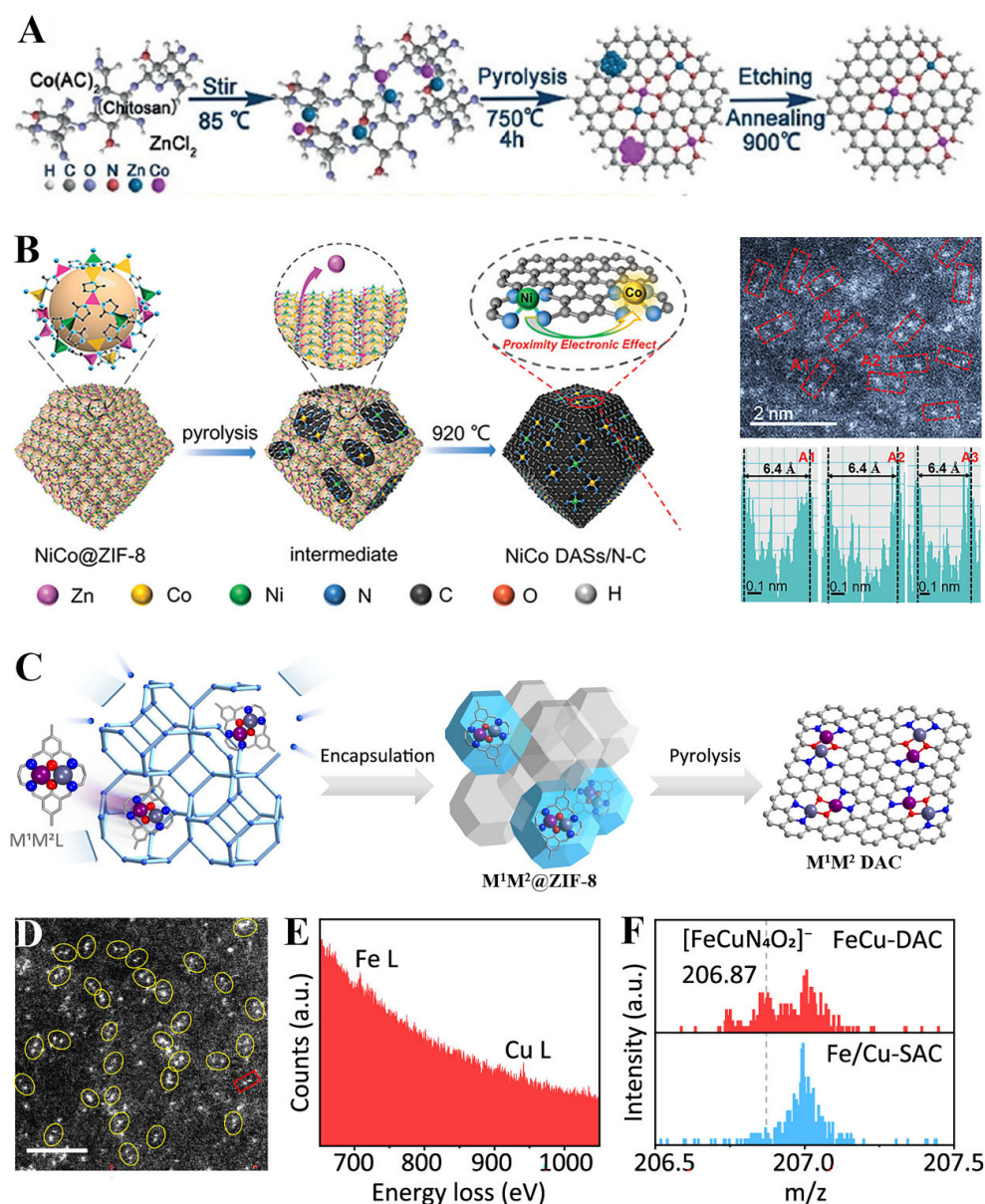


Figure 4. (A) The preparation process for Zn/CoN-C. Reproduced with permission from Ref.^[79]. Copyright 2019, Wiley-VCH; (B) Scheme of the synthesis process of NiCo DASs/N-C. Reproduced with permission from Ref.^[81]. Copyright 2022, Wiley-VCH; (C) Macrocyclic precursor-mediated encapsulation-pyrolysis to prepare DACs; (D) AC HAADF-STEM image of FeCu-DAC and the scale bar is 2 nm; (E) EELS of a FeCu dual atoms as labeled in the red rectangle in Figure 4D; (F) TOF-SIMS spectra of FeCu-DAC and Fe/Cu-SAC; (C-F) Reproduced with permission from Ref.^[87]. Copyright 2023, American Chemical Society. DACs: Dual-atom catalysts; AC HAADF-STEM: aberration-corrected high-angle annular dark-field scanning transmission electron microscopy; TOF-SIMS: time-of-flight secondary ion mass spectrometry.

on the NC substrate were fabricated [Figure 4B]^[81]. First, Ni and Fe atoms were encapsulated in the ZIF-8 owing to the atom size matching. Then it was pyrolyzed under N_2 at 920 °C to evaporate Zn atoms, resulting in the $Ni-N_4$ and $Co-N_4$ moieties uniformly dispersed on carbon substrate. The bright spots in AC HAADF-STEM indicated the presence of NiCo dual atoms, and the distance of atomic pairs was about 6.4 Å [Figure 4B]. It was demonstrated that $Co-N_4$ was the dominant active center, and the adjacent $Ni-N_4$ was a modulator to tune the electronic localization of $Co-N_4$ for synergistically enhancing oxygen reduction reaction (ORR) and hydrogen evolution reaction (HER) processes. Under the two-solvent route, the Fe-doped ZIF-8 was first prepared, where Fe ions were bonded to the ligand as nodes. Then, the Fe-doped

ZIF-8 was dispersed in n-hexane to adsorb nickel nitrate, and nickel nitrate could be encapsulated within the ZIF-8 cavities. Finally, the Ni/Fe-N-C was formed by thermal pyrolysis at 1,000 °C^[82]. Furthermore, Li *et al.* used ZIF-8-derived NC as the substrate to simultaneously adsorb Ni and Fe ion pairs, and N-bridged Ni-Fe dual sites were obtained after pyrolysis at 900 °C^[83]. The synergy between Ni and Fe sites enabled optimal *COOH adsorption and *CO desorption, improving CO₂ reduction performance. Besides, Liu *et al.* proposed *in situ* encapsulation of FeCo phthalocyanine dimer into ZIF-8 followed by pyrolysis to prepare DACs with adjacent FeN₄ and CoN₄ configurations^[84]. Moreover, COFs are also ideal hosts for loading dual atoms due to their high porosity and open channels. The Zn-Co dual atoms were synthesized via *in situ* synthesis of ZIF in the pores of COFs and subsequent pyrolysis^[85]. In addition, the metal-triazolate framework (MET-6) was an attractive precursor for the preparation of Mn and Co dual atoms, which enhanced Fenton-like reaction activity^[86]. These studies suggest that the type of MOFs and loading sequence could influence the configuration of DACs and coordination environment. In general, one metal is anchored as the node and the other is coordinated by a ligand via a two-solvent route, producing dual atoms with direct metal-metal coordination.

Apart from heteronuclear DACs, homonuclear DACs can also be obtained based on an encapsulation-pyrolysis strategy. For instance, Zhang *et al.* developed a general approach for developing a DAC library in a wide range of homonuclear (Fe₂, Co₂, Ni₂, Cu₂, Mn₂, and Pd₂) and heteronuclear (Fe-Cu, Fe-Ni, Cu-Mn, and Cu-Co) bimetal centers^[87]. As displayed in Figure 4C, a binuclear complex M¹M²L was used as a precursor, which was confined by the pores of ZIF-8. The pyrolysis was at 900 °C to carbonize the M¹M²L@ZIF-8 and yield DACs. The AC HAADF-STEM image revealed the atomically dispersed metal sites [Figure 4D], which were further confirmed to be Fe and Cu atoms by electron energy-loss spectroscopy (EELS) in Figure 4E. In other evidence, they performed time-of-flight secondary ion mass spectrometry (TOF-SIMS) to analyze the mass fragments. The diatomic fragment of [FeCuN₄O₂]⁺ held a higher intensity in FeCu-DAC compared to Fe/Cu-SAC [Figure 4F], suggesting a similar structure between FeCu-DAC and [FeCuN₄O₂]⁺ complex. This work opens a new way of using polynuclear complexes to construct a large variety of DACs. Besides, Leng *et al.* constructed dual atoms (Fe, Cu, or Ir) derived from metal dimer functionalized MOFs^[88]. First, the metal dimer was immobilized on the surface of CTAB-functionalized ZIF-8. Second, the sample was coated with polydopamine to inhibit thermal atomic migration. The Fe pairs were anchored on a cubic nanocage with the formation of well-defined N-coordinated Fe₂ atoms, which exhibited superior activity for ORR. Moreover, the coordination environments of Ni₂ DACs were modulated by the control of pyrolysis temperature. Three Ni₂-NC catalysts including Ni₂-N₇, Ni₂-N₅C₂, and Ni₂-N₃C₄ were synthesized by pyrolysis at 700, 800, and 900 °C^[45]. As a result, Ni₂-N₃C₄ showed the highest electrochemical CO₂ reduction activity, which originated from the electronic state change to the Ni center and the appropriate adsorption strength of key intermediates. However, a considerable amount of single atoms was yielded along with DACs. Therefore, great attention should be given to ensuring that pyrolysis proceeds in a more controlled way. Additionally, the pyrolysis will cause a part of active metals embedded in the bulk of the matrix materials. The construction of ultrathin substrates is a promising strategy to enable dual-metal site exposure and boost catalysis.

Atom trapping

The atom trapping approach, originally designed for the synthesis of thermally stable single-atom Pt on ceria, has recently been illustrated as effective for fabricating DACs as well. This method makes use of the abundant oxygen vacancies in reducible substrates, such as CeO₂. By aging in the air at 800 °C, the Pt group metals emitted as metal oxides migrated and then were trapped by substrate with defect sites^[89]. As presented in Figure 5A, Pt and Pd dual atoms were anchored on vacancy-rich CeO₂, which exhibited outstanding three-way catalysis performance^[90]. The AC HAADF-STEM image revealed Pt and Pd in pairs dispersed on the surface of CeO₂ [Figure 5B]. Furthermore, the extended X-ray absorption fine structure (EXAFS) spectra

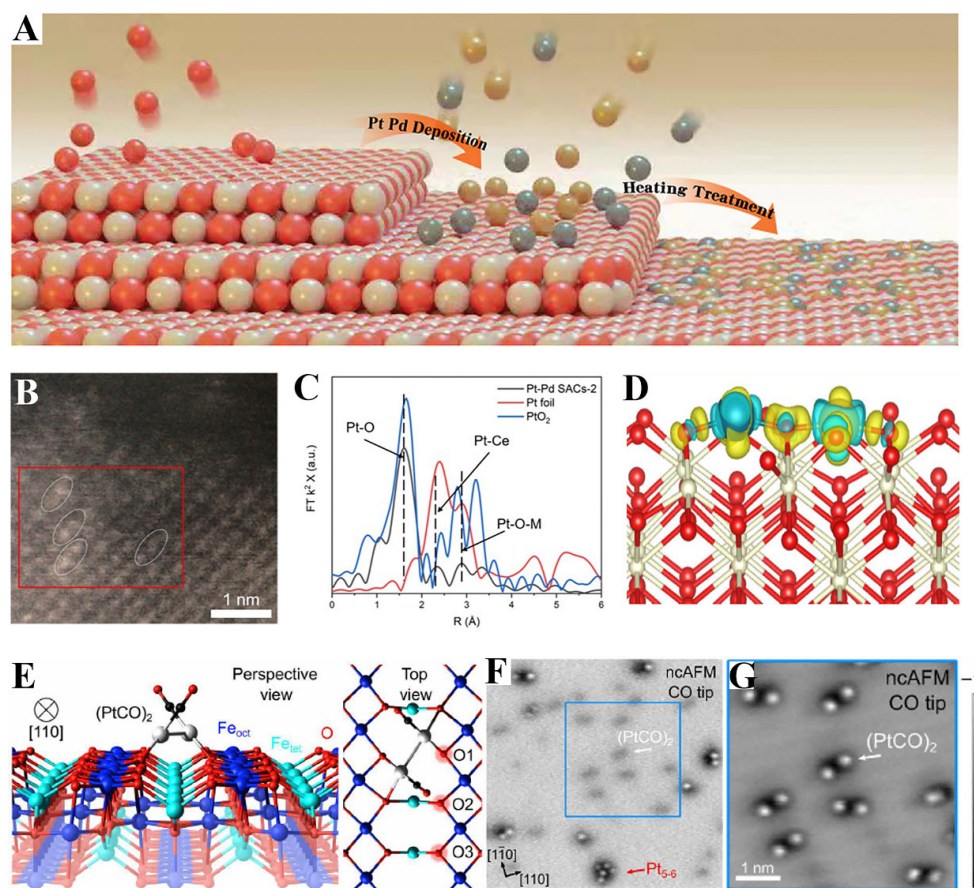


Figure 5. (A) The method for preparing Pt-Pd DAC; (B) HAADF-STEM image of Pt-Pd DAC; (C) EXAFS spectra in the R space of Pd K-edge; (D) Charge density of Pt-Pd DAC; (A-D) Reproduced with permission from Ref.^[90]. Copyright 2022, Wiley-VCH; (E) Perspective and top view of the $(\text{PtCO})_2$ dimer on $\text{Fe}_3\text{O}_4(001)$; (F) Constant-height ncAFM image taken with a CO-functionalized tip; (G) Constant-height ncAFM image of the $(\text{PtCO})_2$ dimers; (E-G) Reproduced with permission from Ref.^[92]. Copyright 2022, American Association for the Advancement of Science. DACs: Dual-atom catalysts; HAADF-STEM: high-angle annular dark-field scanning transmission electron microscopy; EXAFS: X-ray absorption fine structure; AFM: atomic force microscopy.

showed peaks including Pt-O, Pd-Ce, and Pd-O-M coordination, indicating the existence of atomic pairs [Figure 5C]. The charge density showed that the abundant delocalized charges gathered along with the Pt-O-Pd bond efficiently lowered the reaction energy barrier [Figure 5D]. The atom trapping has also been verified to be versatile. Pd_1 and Rh_1 dual atoms were developed by calcining the PdPh@CeO_2 precursor in air at 700°C ^[91]. The synergistic interaction between adjacent Pd and Rh demonstrated a remarkable improvement in methane combustion. Besides, metal dimers could be generated dynamically under the reaction condition. Meier *et al.* investigated CO oxidation by a model $\text{Pt/Fe}_3\text{O}_4$ and found that $(\text{PtCO})_2$ dimers produced via the agglomeration of mobile Pt-carbonyl species^[92]. Each Pt atom was bonded to two oxygen atoms on adjacent rows of the substrate structure [Figure 5E]. Noncontact atomic force microscopy (AFM) displayed the Pt_2 species as faint dark protrusions [Figure 5F]. When the tip was closer, two bright protrusions appeared above each Pt_2 dimer [Figure 5G]. This study manifests that metastable active species can be formed under a reaction environment and the introduction of just one atom can make a significant difference to SACs.

In short, we summarize the preparation approaches for achieving dual-atom dispersion, including ALD, wet-chemistry method, high-temperature pyrolysis, and atom trapping. Each strategy has its superiority and drawbacks and may be suitable for particular cases. Among the various methods, the ALD technique shows a

Table 1. Summary of synthesis strategies, active center structures, and catalytic applications for DACs

Catalysts	Active center structures	Synthesis strategies	Applications	Ref. (year)
PdCu-NC	Pd-N ₄ , Cu-N ₄	electrochemical reduction method	ethylene glycol oxidation	2022 ^[93]
PtFe-NC	Pt-N ₄ , Fe-N ₄	high-temperature pyrolysis	ORR	2021 ^[94]
NiFe-NC	Ni-N ₄ , Fe-N ₄	high-temperature pyrolysis	CO ₂ RR	2021 ^[95]
CuCo-NC	Cu-C ₄ , Co-N ₄	misplaced deposition strategy	oxidative esterification	2021 ^[96]
NiCo-NC	Ni-N ₄ , Co-N ₄	two-step pyrolysis	CO ₂ RR	2023 ^[97]
FeMn-NC	N ₂ Fe-N ₂ -MnN ₂	molten salt assisted pyrolysis	ORR and OER	2022 ^[98]
NiFe-NC	N ₂ Ni-N ₂ -FeN ₂	adsorption and pyrolysis	CO ₂ RR	2024 ^[99]
NiCo-NC	N ₂ Ni-N ₂ -CoN ₂	assembly and carbonization	polysulfide conversion	2024 ^[100]
ZnCo-NC	N ₂ Zn-N ₂ -CoN ₂	competitive complexation strategy	propane dehydrogenation	2023 ^[101]
CuFe-NC	N ₂ Cu-ON ₂ -FeN ₂	assembly and pyrolysis	electrochemical NO reduction	2023 ^[102]
CuNi-NC	N ₂ Cu-S-NiN ₂	co-impregnation method	CO ₂ RR	2024 ^[103]
CoNi-NC	N ₃ Co-NiN ₃	coating and pyrolysis	ORR and OER	2019 ^[104]
CuSn-NC	N ₂ Cu-SnN ₂	dissolution and carbonization method	CO ₂ RR	2023 ^[105]
CuZn-NC	N ₃ Cu-ZnN ₃	high-temperature pyrolysis	acetylene semihydrogenation	2024 ^[106]
NiCu-NC	N ₃ Ni-CuN ₃	host-guest strategy	CO ₂ RR	2022 ^[107]
FeSn-NC	N ₂ Fe-SnN ₂	two-step pyrolysis	ORR	2024 ^[108]

DACs: Dual-atom catalysts; ORR: oxygen reduction reaction; OER: oxygen evolution reaction.

high level of precision in controlling the catalysts. Although there is an advantage in uniformity and atomic-scale regulation, the high cost limits its large-scale fabrication. Besides, the high-temperature atmosphere can lead to atom sintering, and deposition conditions usually depend on experience. For the precursor-preselected wet-chemistry method, the preparation of dinuclear precursors is complicated and the type of metal complexes is limited. High-temperature pyrolysis is usually used to synthesize dual atoms on NC materials. It is worth noting that the uniformity of samples is difficult to control, and such an approach can also result in a part of the active metals embedded in the bulk of the substrate matrix, making it hardly accessible during the reaction process. The atom trapping technique has a requirement for support, usually being appropriate for reducible oxides with abundant vacancies. Therefore, the selection of proper metallic precursors, reaction atmosphere, and temperature is critical to obtaining uniformly dispersed dual atoms.

THE ACTIVE CENTER STRUCTURE OF DACs

Precise identification of active center structures of DACs is difficult but significant for the study of the structure-activity relationship. To verify the successful synthesis of DACs, characterization at the atomic scale is urgently needed. Due to the flexible coordination structure of DACs, it brings more difficulties in the identification of the local environment and electronic configurations. In recent years, advanced techniques have been developed to enable atomic-level interrogation of the nature of dual-atom structures. Here, we focus on several techniques that are sensitive to the dual-atom structures, such as AC HAADF-STEM, X-ray absorption spectroscopy, *in situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS), and other modern sophisticated techniques. The AC HAADF-STEM is a critical tool to provide the direct observation of dual-atom dispersion. XAFS is used to illustrate the electronic structure and coordination environment of metal atoms. Moreover, infrared spectroscopy is also important in characterizing single or dual atoms through special probe molecular adsorption. It is significant to combine various characterization techniques to clarify the structure of dual metal atoms and explore their unique performance. The synthesis strategies, active center structures, and catalytic applications for DACs are summarized in Table 1.

DACs with non-bonding interaction

Identification and understanding of the long-range interaction between neighboring single-metal atoms is of great significance to catalysis. Moges *et al.* prepared Pd-N₄/Cu-N₄ sites by an electrochemical reduction method^[93]. The coordination structure was confirmed by EXAFS fitting results. The synergetic properties of the Pd-N₄ acted as an active center and Cu-N₄ served as a structural site, which showed outstanding reactivity for ethylene glycol electrooxidation. Besides, the adjacent Pt-N₄ moiety was considered to tune the 3d electronic orbitals of the Fe-N₄ center to improve ORR activity^[94]. Based on the EXAFS spectra, the isolated Pt-N₄ and Fe-N₄ structure was confirmed. Moreover, they found that this modulation effect was not effective in optimizing the ORR performance of Co-N₄/Pt-N₄ and Mn-N₄/Pt-N₄. In addition, Jiao *et al.* constructed a new Fe₁-Ni₁-N-C with a non-bonding interaction of adjacent Fe and Ni dimers for CO₂ electroreduction^[95]. As presented in Figure 6A, NC embedded by neighboring Fe-N₄ and Ni-N₄ was synthesized via pyrolysis. The atomic-resolution EELS line scan showed an atomic pair containing one Fe atom and one Ni atom, strongly verifying the formation of Ni-Fe dual atoms [Figure 6B]. To further distinguish the microenvironment, the EXAFS fitting showed isolated Fe-N₄ and Ni-N₄ configurations with an interatomic distance of about 4.1 Å [Figure 6C]. Wang *et al.* exploited a simple method to fabricate isolated FeCo-NC catalysts^[109]. Specifically, they used ZIF-8 to adsorb Fe(acac)₃ and Co(acac)₃ solutions and the obtained precursors were subsequently pyrolyzed at 900 °C under 5% H₂/Ar atmosphere. It was confirmed to be Fe-N₄ and Co-N₄ configurations from EXAFS fitting. Based on a typical M-N₄ structure, Yang *et al.* synthesized FeCu DACs on commercial carbon black^[110]. The EELS validated the co-existence of Fe and Cu atoms. The EXAFS fitting further indicated that both Fe and Cu atoms were bonded to four N atoms as Fe-N₄ and Cu-N₄ configurations. The introduction of Cu as a promoter lowered the energy barrier for the ORR process.

Inspired by theoretical calculations, Tamtaji *et al.* designed graphene-supported DACs in FeMN₆ and FeMN₈ configurations (M:Fe, Co, Ni, Cu, and Zn)^[111]. Importantly, the non-bonding interaction of these counterpart metals could change the ORR activity of Fe sites. The FeNi-N₈ structure demonstrated a superior activity comparable to the benchmark Pt/C. This work suggests a DFT-guided strategy for designing FeM-NC DACs for electrochemical reactions. Apart from Fe-based DACs, Cu and Zn dual-metal atoms were observed to promote ORR. For instance, Tong *et al.* constructed an atomically dispersed Cu-N₄ and Zn-N₄ on NC substrate by pyrolyzing a CuZn-ZIF precursor^[112]. Operando X-ray absorption near edge structure (XANES) showed that the Cu-N₄ as an active site underwent the change from atomic dispersion to cluster with the synergy of Zn-N₄ during the reaction process, and then turned to single atoms again after the reaction. The low electronegativity Zn atom could transfer electrons to Cu, facilitating the cleavage of O-O on Cu-N₄ sites. In addition, Bi/Zn DACs featuring Bi-N₄ and Zn-N₄ moiety were effective for syngas production with controlling CO/H₂ ratios from 0.20 to 2.92^[113]. Zhao *et al.* reported a misplaced deposition strategy for the construction of differently coordinated DACs^[96]. As proof of the concept, they fabricated the Cu and Co dual atoms. The charge distribution pattern [Figure 6D] was simulated to reveal the electrical properties of Cu and Co sites. The as-prepared catalyst with the asymmetric deployment of CuC₄ and CoN₄ sites led to a greatly polarized surface charge distribution including both electron-rich CuC₄ and electron-deficient CoN₄ sites. The EXAFS fitting and wavelet transform results confirmed the CuC₄ and CoN₄ structure [Figure 6E-F]. This finding may open new avenues for designing DACs with coexistent electron-rich and electron-deficient sites for efficient synergistic catalysis. Except for Co and Cu dual atoms, other metals such as Ni can also modulate selectivity and optimize the electrochemical CO₂ reduction to syngas. It was reported that the ratio of CO/H₂ could be controlled by tuning the Co/Ni ratio in individual NiN₄ and CoN₄ dual sites^[97]. This work offers a new way to achieve industrial-level syngas production by CO₂ electroreduction.

Recently, some studies have also focused on S doping, and results showed the charge redistribution of central metal atoms owing to the different electronegativity compared to N species. In this case, Chen *et al.* design

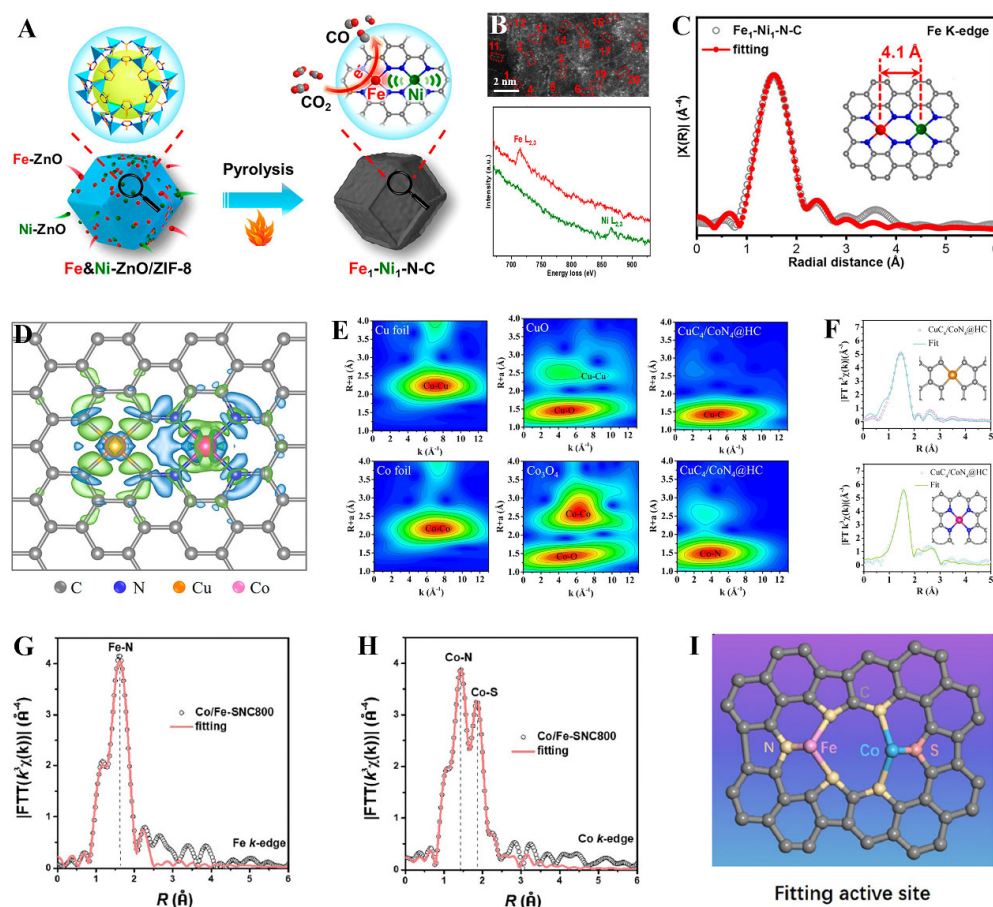


Figure 6. (A) Preparation of Fe₁-Ni₁-N-C on ZIF-8; (B) AC HAADF-STEM image and EELS spectra; (C) Fe K-edge EXAFS spectrum fitting and (inset) optimized configuration; (A-C) Reproduced with permission from Ref.^[95]. Copyright 2021, American Chemical Society; (D) Top view of the differential charge densities of Cu₄/CoN₄@HC; (E) Wavelet-transformed k^3 -weighted EXAFS spectra of Cu/Co foil, CuO, Co₃O₄, and Cu₄/CoN₄@HC; (F) Cu/Co K-edge EXAFS fitting curves; (D-F) Reproduced with permission from Ref.^[96]. Copyright 2021, American Chemical Society; (G) Fe k-edge EXAFS fitting; (H) Co k-edge EXAFS fitting; (I) Model of fitting active site; (G-I) Reproduced with permission from Ref.^[114]. Copyright 2023, The Royal Society of Chemistry. AC HAADF-STEM: Aberration-corrected high-angle annular dark-field scanning transmission electron microscopy; EELS: electron energy-loss spectroscopy; EXAFS: extended X-ray absorption fine structure.

Co-Fe dual toms to optimize OER performance^[114]. As presented in Figure 6G-H, the R-space fitting results of Fe and Co K-edge indicated atomically dispersed Fe and Co species, where the configuration was revealed to FeN₃ and CoN₂S coordination structure [Figure 6I]. The interplay between Fe and Co sites was a key factor for improved oxygen evolution reaction (OER) activity, where the Co atom bound with S and N enabled efficient site-to-site electron transfer, while the Fe atom bound with N facilitated stability of the Co site. In the other study, the reversed electron transfer mechanism on Au and Co DACs was reported^[115]. The coordination number of Au-S and Co-S was about 2 and 4, respectively. It was revealed that the localized electrons around Co and delocalized electrons from Au created a polarized region to boost CO₂ reduction.

DACs with N/O/S/Cl-bridged interaction

The geometry configurations and electronic states are the most critical factors to optimize reaction performance. At present, some attention has been paid to different active structures of DACs, especially nonmetallic atoms (e.g., N, O, S, Cl, *etc.*) bridged dual-metal atoms. Yang *et al.* implanted Mn-N moiety in

Fe-N-C to prepare FeMn-N-C atomic pairs, where dicyandiamide was used as C and N sources, and FePc and manganese nitrate were used as metal precursors^[116]. On the basis of the simulated Fe K-edge spectra of XANES and the calculated structural model, the FeMn-N₆ structure was suggested as the most possible configuration for an as-prepared catalyst. The introduction of the Mn-N site caused Fe^{III} electron delocalization and made the spin state of Fe^{III} transition from low spin ($t_{2g}^5e_g^0$) to intermediate spin ($t_{2g}^4e_g^1$), readily penetrating the antibonding π -orbital of oxygen and achieving the outstanding ORR activity. Most previously reported NC supports for anchoring DACs show three-dimensional (3D) bulk structures, making lots of active sites buried inside and insufficient mass transfer. To address this, Cui *et al.* designed N-bridged Fe-N₄ and Mn-N₄ sites dispersed on ultrathin two-dimensional NC nanosheets with porous architecture, which exhibited excellent bifunctional activities for ORR and OER^[98]. In a similar case, the FeNi-N₆ configuration was found effective in acidic ORR than its single-atom counterpart^[117]. Most recently, Chen *et al.* reported the effect of Ni and Fe atomic distance on the performance of CO₂ electroreduction [Figure 7A]^[99]. They designed three different configurations with NiFe-isolate, NiFe-N bridge, and NiFe-bonding to tune the dual-atom distance. The AC HAADF-STEM images of NiFe-N bridge illustrated atomically dispersed Ni and Fe atoms [Figure 7B]. As shown in Figure 7C, atomic resolution EELS further confirmed that the dual-atom ensemble comprised one Ni atom and one Fe atom. Various characterizations and theoretical calculations suggested that two N-bridged Ni and Fe atoms with an optimal dual-metal distance facilitated *COOH adsorption and promoted CO desorption, thus enhancing performance. This finding not only sheds light on the distance effect in DACs but also provides a fundamental understanding of dual-atom interaction, which can be helpful for optimizing catalytic performance. Moreover, Wang *et al.* tailored the d-band electronic energy of the Ni center through introduction of the Zn atom, enhancing the Ni-OOH* adsorption and leading to high activity for H₂O₂ production^[118]. Based on the XAFS analysis, the local structure was identified to comprise Ni-N₄ and axial Zn-N₃ moieties within a carbon framework. Besides, the adjacent Cu-N₄ site could also induce the charge redistribution of Ni species, lowering the formation barrier of *COOH on Ni-N₄ sites and promoting CO production^[119]. Additionally, the N-coordinated Ni-Cu DAC showed good performance for nitrate reduction to ammonia^[120]. The interaction of Ni and Cu dual atoms and the strong hybridizations of Cu 3d and Ni 3d-O 2p orbitals of NO₃⁻ played a pivotal role in NH₃ synthesis.

In the NiCo-NC system, the presence of Ni and Co atom pairs alongside N-bridged Ni-N₄ and Co-N₄ coordination environments was observed^[100]. The NiCo-NC DAC demonstrated exceptional activity in the conversion of lithium polysulfide, indicating promising prospects for lithium-sulfur batteries. Very recently, two N-bridged Fe-N₄ and Co-N₄ diatomic sites were developed for Zn-air/iodide hybrid batteries^[121]. The strong coupling between 3d orbitals of Fe and Co weakened the binding strength between active sites and intermediates, promoting the activities for both ORR/OER and iodide/iodate redox. The N-colligated Zn₁Co₁ dual atoms were found as the main active sites for high-temperature propane dehydrogenation (PDH)^[101]. The role of N-colligated Zn₁Co₁ species was further disclosed, which originated not only for the coordination of N atoms for C-H bond scission but also for the feasible channel for C₃H₆ desorption via the retrofitted Co₁ site neighboring with Zn₁ site. An important work reported that the activity of CuCo DACs for ORR, OER, and HER processes was determined by coordination shells. By controlling the amount of thiomalic acid in the precursors, three DACs with unique coordination structures were constructed as S atoms that directly bond to CuCo-N₆ in the lower coordination shell, indirectly bond in the neighboring coordination shell, and doped in the higher coordination shell, respectively^[122]. Interestingly, the direct bonding of S made Cu with a comparatively low chemical state of + 1.6, promoting ORR. The indirect bonding of S resulted in a moderate chemical state (e.g., Cu + 1.8), improving OER. When S atoms were located at greater distances, the metal atoms showed a higher chemical state (e.g., Cu + 2.0), promoting HER. These findings offer a new strategy to design highly efficient DACs by tuning the coordination environments beyond the first shell for diverse applications.

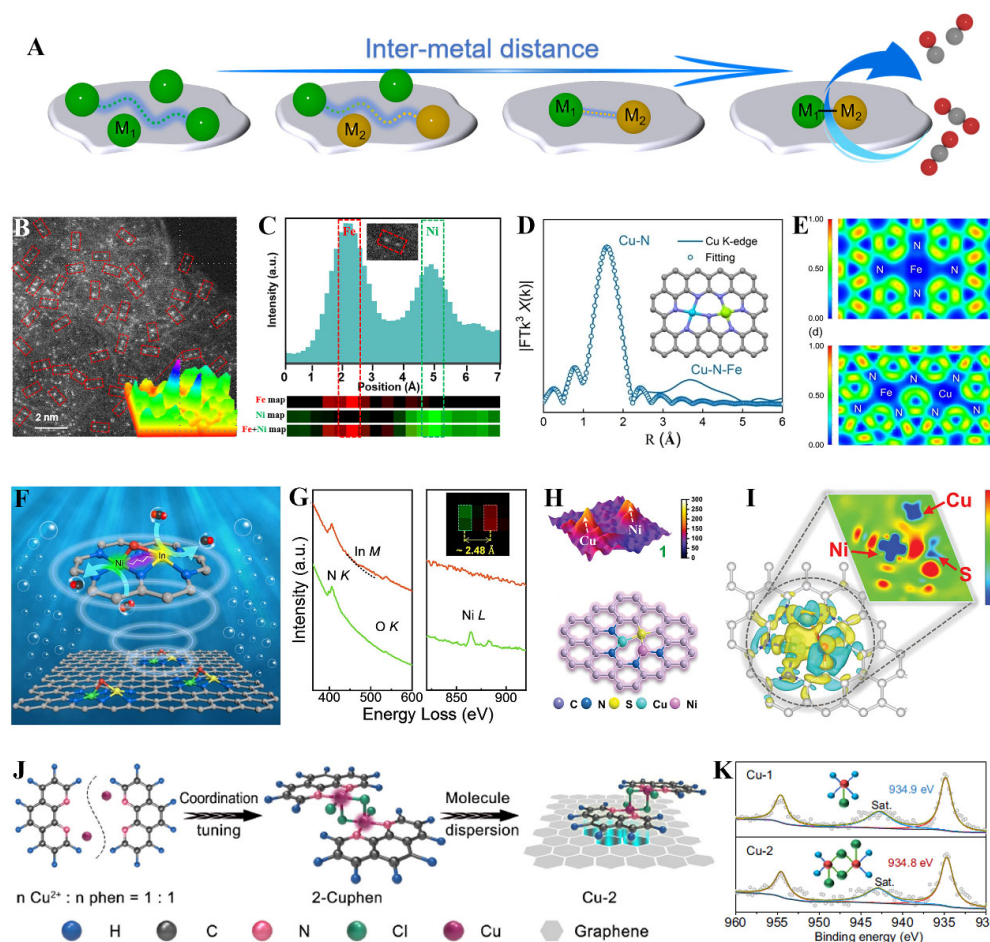


Figure 7. (A) Schematic of DACs showing the distance change of inter-NiFe on different models with SAC as a comparison; (B) AC HAADF-STEM image of NiFe-N bridge and 3D intensity surface plot; (C) Atomic resolution EELS mapping of NiFe-N bridge; (A-C) Reproduced with permission from Ref.^[199]. Copyright 2024, Wiley-VCH; (D) R-space curve-fitting and corresponding fitted structure of the Fe and Cu atoms; (E) ELF analysis for FeN₄ and FeCuN₃; (D-E) Reproduced with permission from Ref.^[123]. Copyright 2024, Wiley-VCH; (F) Illustration of axial oxygen bridged In-N₆-Ni structure for electrochemical CO₂ reduction; (G) The EELS spectra of In-Ni atomic pair; (F-G) Reproduced with permission from Ref.^[124]. Copyright 2023, Wiley-VCH; (H) 3D model of Cu-S-Ni sites and structural model of Cu-S-Ni/SNC; (I) Electron density difference plot of Cu-S-Ni site; (H-I) Reproduced with permission from Ref.^[103]. Copyright 2024, Wiley-VCH; (J) The preparation for Cu-2; (K) Cu 2p XPS spectra; (J-K) Reproduced with permission from Ref.^[128]. Copyright 2024, Springer Nature. DACs: Dual-atom catalysts; AC HAADF-STEM: aberration-corrected high-angle annular dark-field scanning transmission electron microscopy; 3D: three-dimensional; EELS: electron energy-loss spectroscopy.

In addition to dual-metal atoms sharing two N atoms, some studies demonstrated that one N-bridged atomic pair was effective in improving reactivity. Bi *et al.* developed a FeCu DAC for direct nitrite reduction to ammonia^[123]. As depicted in Figure 7D, the EXAFS fitting analysis revealed the existence of N₃Fe-N-CuN₃ configuration. In light of this evidence, the electron localization function (ELF) was performed to further reveal the degree of electronic delocalization of N₃Fe-N-CuN₃. As plotted in Figure 7E, the N₃Fe-N-CuN₃ configuration showed a larger region area around Fe-N atoms than that of Fe-N₄ in ELF, suggesting that the N₃Fe-N-CuN₃ possessed richer delocalized electrons. The introduction of Cu atoms changed the energy of the Fe 3d orbital and decreased the reaction barriers, promoting the nitrite reduction reaction. Besides, it was found that one N-bridged CoNi DAC (N₃Co-N-NiN₃) achieved 95% polystyrene conversion and 92% ethylbenzene yield, greatly higher than the corresponding SACs^[80]. The experimental results and theoretical calculations revealed that the Co site could activate the C=C bond easily, while the Ni site spatially optimized the adsorption configuration of the styrene owing to the electronic interplay. To further regulate the electronic properties and local environment of DACs, Gong *et al.* regulated the coordination structure

around Ni₂ centers by changing pyrolysis temperatures^[45]. It was disclosed that the C₂NNi-N-NiNC₂ structure significantly boosted activity for CO₂ electroreduction to CO. This finding provides a way to boost catalytic performance via tailoring the local environments of DACs.

Except for N-bridged configuration, O-bridged dual atoms are also efficient for enhanced catalysis. For instance, Fan *et al.* designed an axial oxygen-bridged indium-nickel DAC with an O-In-N₆-Ni configuration [Figure 7F]^[124]. The EELS spectra extracted from the two labeled regions confirmed the atomically dispersed In and Ni species [Figure 7G]. *In situ* attenuated total reflection surface-enhanced infrared absorption spectroscopy (ATR-SEIRAS) combined with DFT results indicated that the synergy of In-Ni dual sites and bridged O atoms not only lowered the reaction barrier for *COOH formation but also inhibited HER. Similarly, an axial oxygen coordinated Cu-Fe DAC as O-Fe-N₆-Cu configuration was efficient for NO electroreduction to NH₃ in neutral electrolyte^[102]. In another work, the O-bridged W-Mo atoms were deposited on N-doped graphene defects featuring W-O-Mo-O-C^[125]. The electron delocalization of this configuration optimized the adsorption strength of H and improved the HER kinetics. Apart from an oxygen-bridged structure, a novel sulfur-bridged Cu-S-Ni DAC was reported with high efficiency for CO₂ reduction^[103]. The 3D intensity map outlined the locations of Cu-S-Ni dual sites and the structural model was depicted as N₂Cu-S-Ni-N₂ [Figure 7H]. As shown in Figure 7I, the charge asymmetry in Cu-S-Ni sites was observed via the electron density difference map. Charge transfer between Cu, S, and Ni atoms emphasized the important regulating role of the S-bridged in electron transfer and charge distribution. It was revealed that Cu as a major active site promoted *COOH formation, thereby achieving superior CO₂ reduction performance. Apart from the S-bridged interaction, the electronic structure of the metal active center can be regulated by the remote interactions of the heteroatoms. The activity of the single Fe-N₄ site could be tuned by incorporating sulfur functionalities into the carbon plane^[126]. The introduction of oxidized sulfur functionality decreased the *d*-band center of irons by withdrawing electrons, thereby lowering the adsorption energy of the intermediate at the Fe-N₄ site and improving the activity. Besides, adjusting the electronic structure of Cu-N₄ sites by heteroatom was investigated^[127]. Experimental and theoretical results indicated that the long-range interaction with B atoms decreased the electronic density of Cu active sites, and optimized the adsorption energy for reactant activation. Impressively, Yang *et al.* developed chlorine-bridged binuclear Cu atoms for lithium-sulfur batteries^[128]. As illustrated in Figure 7J, the 2-Cuphen complex was first prepared by tailoring the mole ratio of Cu²⁺ and 1,10-phenanthroline ligand into 1:1. Subsequently, the obtained Cu complex was supported on a graphene substrate for fabricating Cu-2 powder. Compared with single-atom Cu, dual-atom Cu displayed a lower binding energy of 934.8 eV, indicating their different coordination environments [Figure 7K]. This DAC harnessing Cl bridge paves a new way to tackle the issues of shuttle effect and dendrite growth in the pursuit of high-performance lithium-sulfur batteries. Based on these studies, apart from common N atoms, O, S, Cl, and other atoms are also promising candidates for regulating the electronic properties and coordination environments of DACs. Interestingly, heteroatom functionalization is also effective in tailoring the electronic properties via long-range interaction.

DACs with direct metal bonding interaction

Recent studies of DACs with metal-metal interaction have achieved great progress in tailoring the configuration and local coordination structure, enabling multiple reaction adsorption sites and outstanding reactivity. For instance, Wang *et al.* designed a new Zn-porphyrin/RuCu-pincer for selective CO₂ photoreduction^[129]. As presented in Figure 8A, the heteronuclear Ru-Cu sites easily promoted C₁ intermediate coupling owing to the strong gradient orbital coupling of Ru4d-Cu3d resonance. The two *CO intermediates of Ru-Cu showed a weaker electrostatic repulsion for an asymmetric charge distribution, which resulted in side-to-side adsorption and lowered the reaction barrier for C-C coupling. In contrast, the homoatomic counterparts exhibited the best selectivity for CO. Besides, covalent triazine frameworks supported the Pd₁-Co₁ catalyst, which was efficient for ambient CO₂ conversion to formate^[130]. It was

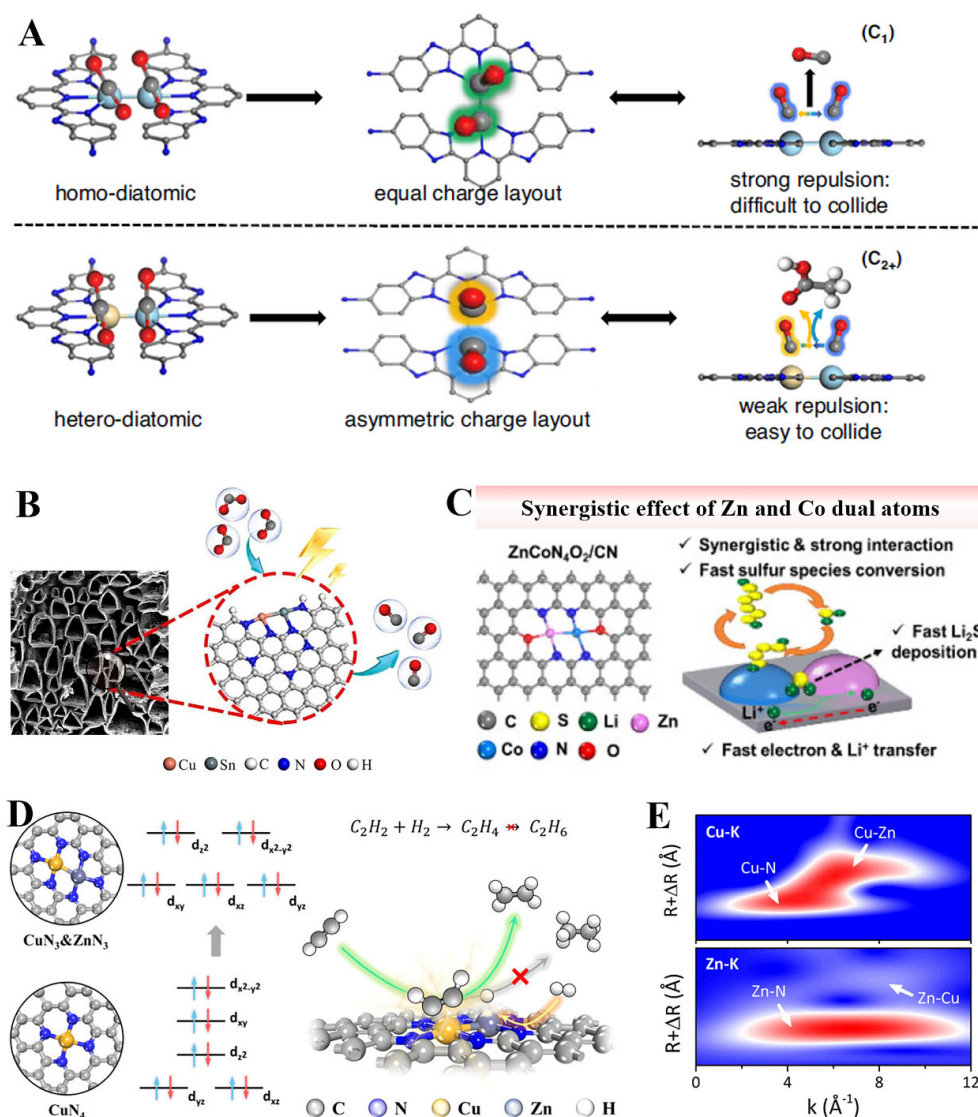


Figure 8. (A) CO₂ reduction mechanism of C₁ and C₂₊ product formation by homo- and hetero-DACs, respectively. Reproduced with permission from Ref.^[129]. Copyright 2023, Springer Nature; (B) Schematic of the Cu-Sn DACs for CO₂RR. Reproduced with permission from Ref.^[105]. Copyright 2023, Springer; (C) Operational principles of ZnCo DAC in Li-S batteries. Reproduced with permission from Ref.^[135]. Copyright 2023, Elsevier; (D) Schematic structures and d-orbital splitting manner for CuZnN₆ and CuN₄; (E) Wavelet transform of Cu and Zn K-edge spectra in CuZn/NC; (D-E) Reproduced with permission from Ref.^[106]. Copyright 2024, American Chemical Society. DACs: Dual-atom catalysts.

revealed that the Pd atom was conducive to the dissociation of hydrogen, and the Co atom facilitated the adsorption and activation of the captured CO₂, leading to a low-energy barrier for CO₂ conversion. Xiao *et al.* developed the Ir-Co dimers for enhanced bifunctional oxygen electrocatalysis^[131]. The introduction of the Ir atom induced a stronger spin polarization of the Co site. It was observed that a significant enhancement of oxygen adsorption on the IrCoN₅ site improved OER/ORR activity.

In addition to noble metal DACs, NC-anchored Fe-Co dual sites were active for ORR under acidic conditions^[42]. The preparation was based on controlling the formation of the N₃Fe-CoN₃ structure. DFT calculations indicated the dual sites were favored for O-O activation, which was important for four-electron ORR. A similar structure was also found to show good ORR activity and durability in alkaline media, promising in practical zinc-air batteries and flexible zinc-zir batteries^[132]. From the viewpoint of theoretical

calculation, a variety of heterogeneous DACs implanted in the graphitic carbon nitride were investigated as the potential candidates for NO₃RR by high-throughput *in silico* first-principles calculations based on DFT^[133]. By testing 21 catalysts, FeMo and CrMo showed a high performance with low limiting potentials for electrochemical NO₃RR. In addition, Co-Ni dual atoms stabilized by N-doped hollow carbon nanocubes with N₃Co-NiN₃ coordination exhibited superior reversibility for ORR/OER^[104]. Atomically dispersed Fe-Ni dual atoms were developed with extraordinary performance for ORR/OER^[134]. DFT calculation revealed that Fe as an active center facilitated four-electron reduction, while the Ni site regulated the electronic properties of Fe and decreased the energy barrier of the rate-limiting step. Recently, asymmetrical FeSn dual atom sites on C₂N nanosheets were developed for ORR^[108]. The p-d orbital hybridization between p-block Sn and d-block Fe triggered electron delocalization and decreased the energy barrier for *OH protonation. Besides, as displayed in Figure 8B, Liu *et al.* introduced Sn into single Cu sites to construct Cu-Sn dual atoms with N₂Cu-SnN₂ for electrochemical CO₂ reduction^[105]. It was suggested that the weakened C-O bonds and the distorted CO₂ configuration promoted CO₂ reduction to CO. As shown in Figure 8C, ZnCoN₄O₂ DACs were synthesized, which could promote Li⁺ transport and Li₂S diffusion, and catalyzed lithium polysulfide conversion more efficiently than homonuclear DACs or single-atom counterparts^[135]. This finding highlights the importance of metal active centers and provides a new approach to designing effective DACs for energy conversion devices. Compared to electrocatalysis, DACs provide excellent selectivity for thermocatalysis, making them attractive candidates for energy conversion. As shown in Figure 8D, Yue *et al.* illustrated the advantages of CuZn dual atoms over the corresponding single atoms in the selective hydrogenation of acetylene^[106]. Wavelet transform results [Figure 8E] showed the Cu-N and Cu-Zn coordination, verifying the formation of the Cu-Zn-N structure. The N₃Cu-ZnN₃ configuration resulted in enhanced d-electro domination near the Fermi level and reordered d-orbital splitting manner, promoting acetylene activation and ethylene desorption.

Compared to heteronuclear DACs, homonuclear DACs with uniform dispersion are more easily obtained, which offers great potential for promoting reactions. For instance, Zhang *et al.* constructed dual-atom Fe on the surface of N-doped graphene for boosting conversion kinetics of Lithium-sulfur batteries^[136]. The as-prepared N₃Fe-FeN₃ catalyst could alleviate the shuttle effect and increase the sulfur utilization; thus, the batteries exhibited high initial capacity and long-cycle life. Furthermore, a unique P₁N₂Fe-FeN₂P₁ coordination structure showed an improved reactivity toward polysulfide conversion owing to the strong coupling between Fe d orbital and S p orbital^[137]. Moreover, Ni₂N₄C₂ DACs were fabricated, and the unique structure of binuclear Ni tailored the electronic property of d-states for the appropriate adsorption of CO₂ and intermediates, achieving high efficiency for CO₂ reduction^[138]. This study provides basic principles for the design of advanced DACs for electrocatalysis.

UNDERSTANDING THE CATALYTIC ROLE OF DACs

With dual metal centers close to each other, DACs possess the advantages of SACs and also present opportunities to tune the interplay between active centers and reactants. The electronic effect is an essential factor affecting the catalytic reaction. Previous studies have stressed the importance of electronic structures of metal active centers on performance^[139,140]. Although a few reviews introduced the spin state change of metal active centers and its effect on electrocatalytic performance^[53]. The nature of spin state change is to influence the electronic properties or charge distribution of metal centers. Generally, dual metal atoms play two types of roles in reactions. On the one hand, one of the metals serves as the active center, and the other metal as a promoter tailors the electronic properties of the active center. On the other hand, dual-metal atoms behave cooperatively to play a bifunctional role, and linear scaling relations may be broken. In this section, we sketch out the current landscape of DACs. In particular, we concentrate on understanding the role of DACs, including electronic effects and synergistic effects, discussing the structure-activity relationship, and providing possible guidelines for the design of efficient catalysts. These effects are typical

and significant for DACs.

Electronic effects

With the promising development of DACs, the chemical interaction between isolated dual atoms has been revealed as a key factor in changing electronic structures and catalytic performance. According to Sabatier's principle, ideal heterogeneous catalysts should have optimized affinity strength between the key intermediates and the surface of a catalyst, which should be neither too weak nor too strong. Constructing an atomic pair structure is regarded as a powerful approach to alter the catalytic behaviors due to the electronic modulation effect. As shown in Figure 9A, the incorporation of Cu positively shifted the Ni 3d orbital energy to the Fermi level, implying an enhanced binding strength of intermediates on the NiCuN₆ sites^[107]. Additionally, the introduction of Cu eliminated the band gap of Ni 3d [Figure 9B], which was considered to lower the energy barrier for intermediate adsorption. As illustrated in Figure 9C, the NiMN₆ dual atoms showed decreased Gibbs free energy for the *COOH formation than the NiN₄ site, while NiCuN₆ promoted *CO desorption, achieving better overall kinetics. Hao *et al.* found the strong electron interactions of Cu and Ni induced by the electronegativity offset^[141]. The averaged and compensated electronic structures optimized the binding strength of *COOH and enhanced CO₂ reduction. Furthermore, a distance threshold of about 5.3 Å between neighboring Ni-N₄ and Cu-N₄ was found to trigger effective electronic modulation and improved activity and selectivity for CO₂ electroreduction^[142]. Moreover, Zhang *et al.* designed a Ni-Cu DAC with a direct bonding structure for CO₂ electroreduction to CO in a wide pH range^[143]. To explore the origin of the enhanced activity, ATR-SEIRAS was used to monitor reaction intermediates. As shown in Figure 9D, the peaks at 1,215 cm⁻¹ were attributed to *COOH intermediate, indicating that CO₂ was easily protonated to generate *COOH on Cu/Ni-NC. The Cu atoms induced the d-band center of Ni closer to the Fermi level than that of Ni in the NiN₃ site, promoting the adsorption of reactants [Figure 9E]. As shown in Figure 9F, the Ni site acted as an active center to adsorb and convert CO₂, and Cu atoms tuned the electronic state of Ni to boost CO₂ reduction. Recently, an asymmetric coordination Fe-Se DAC was designed for CO₂ electroreduction to CO^[144]. It was demonstrated that the electronic hybridization effect induced by asymmetrically coordinated Fe-Se dual sites enhanced the adsorption of *COOH and promoted the desorption of *CO, leading to excellent CO₂ reduction performance. This work provides valuable insights into the design of highly efficient DACs through the electronic hybridization effect.

In addition to NiCu DACs, Xie *et al.* developed a NiSn atomic pair for CO₂ reduction to formate^[145]. Different from the NiCu system, it was verified that Sn served as the intrinsic active center and the neighboring Ni site imposed the electron redistribution of Sn. This facilitated the formation of *OCHO intermediate and made the potential-determining step thermodynamically spontaneous. Besides, main-group metal In could tune the electronic property of the neighboring Cu site to boost CO₂ reduction to CO without the HER side reaction^[146]. The electronic donation effect of electron-rich Cu sites strengthened the adsorption of *COOH on Cu sites and enhanced activity. Except for experimental explorations, significant efforts have been devoted to catalyst screening via theoretical calculations. Taking Fe SAC as an example, it was demonstrated that the design of a dual-atom center by the introduction of Cu allowed for CO₂ reduction to produce CH₃OH and CH₄^[147]. Theoretical results suggested that Fe served as the active site and Cu acted as the promoter to enhance activity, which promoted the formation of multi-electron products. The theoretical prediction will simulate experiments to fabricate excellent DACs for CO₂ reduction to high-value chemicals. Although some progress has been made, the choice of metal of dual atoms as the main active center is still controversial. It is worth making great efforts to explore more DACs to understand the origin of differences in electronic structures.

Constructing dual-metal atoms may open a new avenue for ORR catalyst design. For instance, dual-metal atoms consisting of Cu-N₄ and Zn-N₄ were constructed^[112]. As presented in Figure 9G, an energy-negative

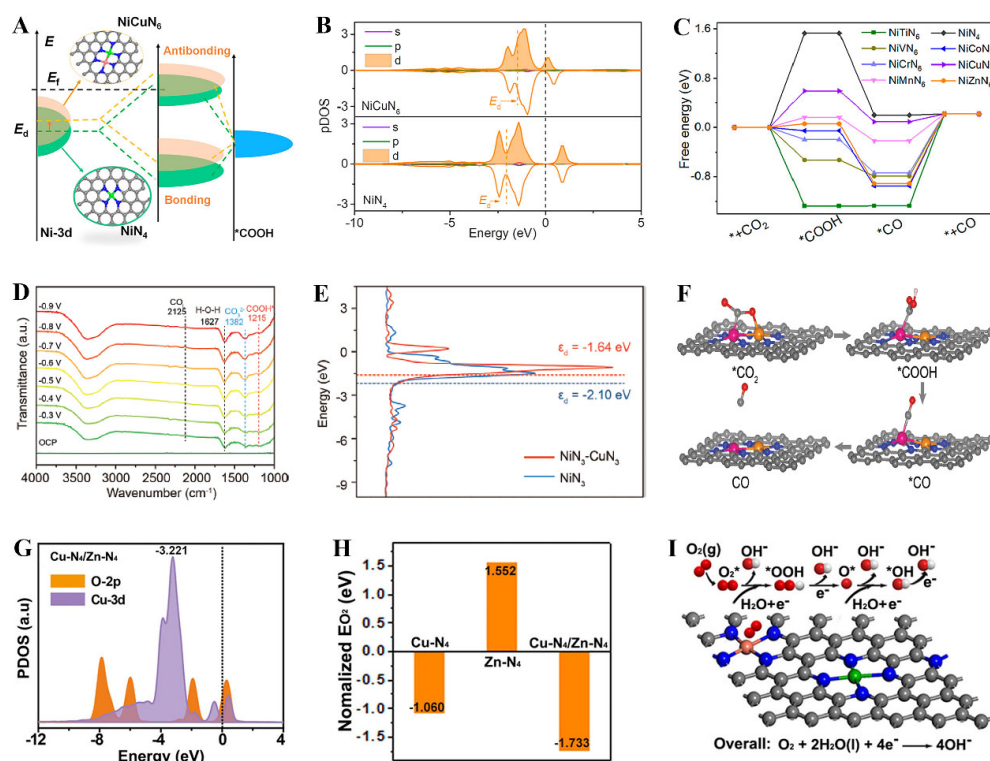


Figure 9. (A) Change of metal-adsorbate interaction by changing the metal d band center; (B) pDOS of Ni in NiN_4 and NiCuN_6 ; (C) Gibbs free energy profiles for CO_2 electroreduction on NiMnN_6 and NiN_4 ; (A–C) Reproduced with permission from Ref. [107]. Copyright 2022, American Chemical Society; (D) *In situ* ATR-SEIRAS test on Cu/Ni-NC in neutral medium; (E) The density of state of Ni d-orbitals in $\text{NiN}_3\text{-CuN}_3$ and NiN_3 ; (F) The CO_2 reduction pathway on $\text{NiN}_3\text{-CuN}_3$; (D–F) Reproduced with permission from Ref. [143]. Copyright 2023, Wiley-VCH; (G) Cu 3d PDOS and O 2p PDOS of $\text{Cu-N}_4/\text{Zn-N}_4$; (H) Free energy for ORR on the three catalysts; (I) Proposed ORR mechanism on the $\text{Cu-N}_4/\text{Zn-N}_4$ site; (G–I) Reproduced with permission from Ref. [122]. Copyright 2021, Wiley-VCH. ORR: Oxygen reduction reaction.

shift of Cu dual-atom structure for O_2 adsorption could be observed, indicating strong adsorption of O_2 on $\text{Cu-N}_4/\text{Zn-N}_4$. Moreover, the O_2 adsorption energy of the dual-metal site was -1.733 eV, smaller than that of the single-atom site [Figure 9H]. After adsorption on the Cu site, the O–O bond was easy to break due to the low electronegativity of Zn that could transfer electrons to Cu. The proposed mechanism of ORR was depicted in Figure 9I. Besides, it was reported that the strain effect caused by CuN_4 replacing the adjacent carbon environment of the FeN_4 could adjust the electronic state and reduce the $^*\text{OH}$ adsorption on FeN_4 sites, boosting the ORR process [148]. Similarly, Li *et al.* reported that the neighboring Ni-N_4 could tune the electronic localization of the Co-N_4 center, facilitating the $^*\text{OH}$ desorption and $^*\text{H}$ adsorption, thus enhancing the ORR and HER process [81]. As for NiMn-NC DAC , it was revealed that the MnN_4 acted as the active center for ORR with the assistance of CoN_4 as electron transfer from Co to Mn [149]. Besides, the addition of the Co-N_4 site into Ru/Co-NC could increase Ru electron density, which then optimized the bonding strength between adsorption species and Ru sites, thus promoting OER and HER [150]. These works provide new insights into the regulation of the electronic nature of dual-atom centers by choosing suitable metal atoms for energy conversion.

The modulation of electronic structure is closely linked to the intrinsic activity of reactions. In one case, one of the metals acts as an electron donator to give electrons to the active metal site. The electron transfer between them may facilitate maintaining the chemical state of active metal and avoiding over-oxidation that would cause catalyst deactivation. In the other case, the introduction of another metal can make the active metal d orbital energy shift to the Fermi level, which promotes the adsorption of key intermediates and

accelerates the rate-limiting step, thus boosting performance. Nevertheless, although DACs possess many advantages, the control of electron transfer direction is still a great challenge. It is difficult to predict dual-atom interaction and the distribution of active sites is not uniform as well. Moreover, electronic regulation is complicated when it involves factors beyond the direct coordination atom, such as the influence of the second shell and further. Therefore, more efforts should be devoted to tailoring dual-atom structures and catalytic properties for heterogeneous catalysis.

In-situ characterizations and theoretical calculations are essential to reveal the active center structures and reaction mechanisms. For instance, ATR-SEIRAS is a critical technique to detect reaction intermediates in electrochemical reactions. Operando ^{57}Fe Mössbauer spectroscopy is effective in evidencing the change from a high-spin Fe(III)Pc to Fe(II)Pc, and *in situ* formation of Fe(II)Pc $^-$ intermediate is observed under CO_2 reduction conditions^[151]. In addition, operando X-ray absorption spectroscopy monitors the dynamic evolution of Cu-N $_4$ to Cu-N $_3$ and further to HO-Cu-N $_2$ under ORR working conditions^[152]. The Cu $^{2+}$ is reduced to Cu $^+$ driven by the applied potential, and low-coordinated Cu $^+$ -N $_3$ is the real active center. Importantly, this finding is supported by DFT calculations. These studies suggest that in-situ/operando characterizations can provide evidence for the dynamic evolution of active site structures and the formation of key intermediates under real reaction conditions, which provide guidance for the calculation of mechanisms. The experimental observation validates the models for theoretical calculations. The reaction pathway and corresponding activation and energy barriers are essential to understanding the reaction mechanisms. There have been several reviews specifically focused on the theoretical insights into mechanisms of various reactions, such as CO_2 reduction and alkane dehydrogenation^[153–155]. These insights will provide theoretical guidance for the rational design of efficient single/dual-atom catalysts for improved catalysis.

Synergistic effects

For DACs, the adjacent atomic metal species can exert a synergistic effect for boosting catalytic performance. For example, Li *et al.* observed synergistic effects of Ni-Zn DAC for the electrochemical CO_2 conversion^[156]. The band gap of Ni 3d orbitals and Fermi level was narrowed and the electronic interaction between the intermediate and active center was enhanced, leading to superior activity for CO_2 electroreduction. Furthermore, Zeng *et al.* reported that the orbital coupling between Fe and Ni resulted in the higher valance state of Fe and weakened adsorption of intermediates, achieving extraordinary activity for both CO_2 reduction and oxygen evolution^[157]. A Ni-Ag DAC was featured as N $_3$ -Ni-Ag-N $_3$ with Faradic efficiency of CO surpassing 90% in a wide range of applied potentials^[158]. It was revealed that the energy barrier of *COOH formation was decreased by the Ni atom, while the Ag atom promoted the *CO desorption. This synergy of DACs offers a promising way for the design of heteronuclear dual atoms for enhanced performance. To further modulate the spatial structure and coordination environment, an S, N-coordination asymmetric Zn-Mn dual site was developed^[159]. Figure 10A showed CO_2 reduction process at Zn-Mn DAC. The chemical states of both Zn and Mn were located between 0 and +2 [Figure 10B]. First-principle calculations disclosed the smaller energy change of CO_2 to *COOH, indicating the facile formation of *COOH via the synergistic role of Zn and Mn sites [Figure 10C]. The difference between the thermodynamic limiting potentials for CO_2RR and HER was calculated to determine the selectivity. The Zn-Mn dual site with a more positive $U_{\text{L}(\text{CO}_2)} - U_{\text{L}(\text{H}_2)}$ value endowed a higher selectivity for CO production [Figure 10D]. Considering the practical application, Yi *et al.* synthesized Co-Cu DACs for synergistic CO_2 electroreduction at a large current density^[160]. The potential dependent step for Co-Cu DACs was CO desorption from metal sites [Figure 10E]. Besides, it exhibited improved selectivity for CO_2RR [Figure 10F]. As presented in Figure 10G, the d band center of Co-Cu DACs is suitable, indicating an appropriate binding strength of *COOH. The cooperative role of Co and Cu sites boosted catalysis. In addition, homonuclear Pd $_2$ -NC and Ni $_2$ -NC also behaved synergistically to improve CO_2 electroreduction performance^[68,70]. Until now, studies on DACs for

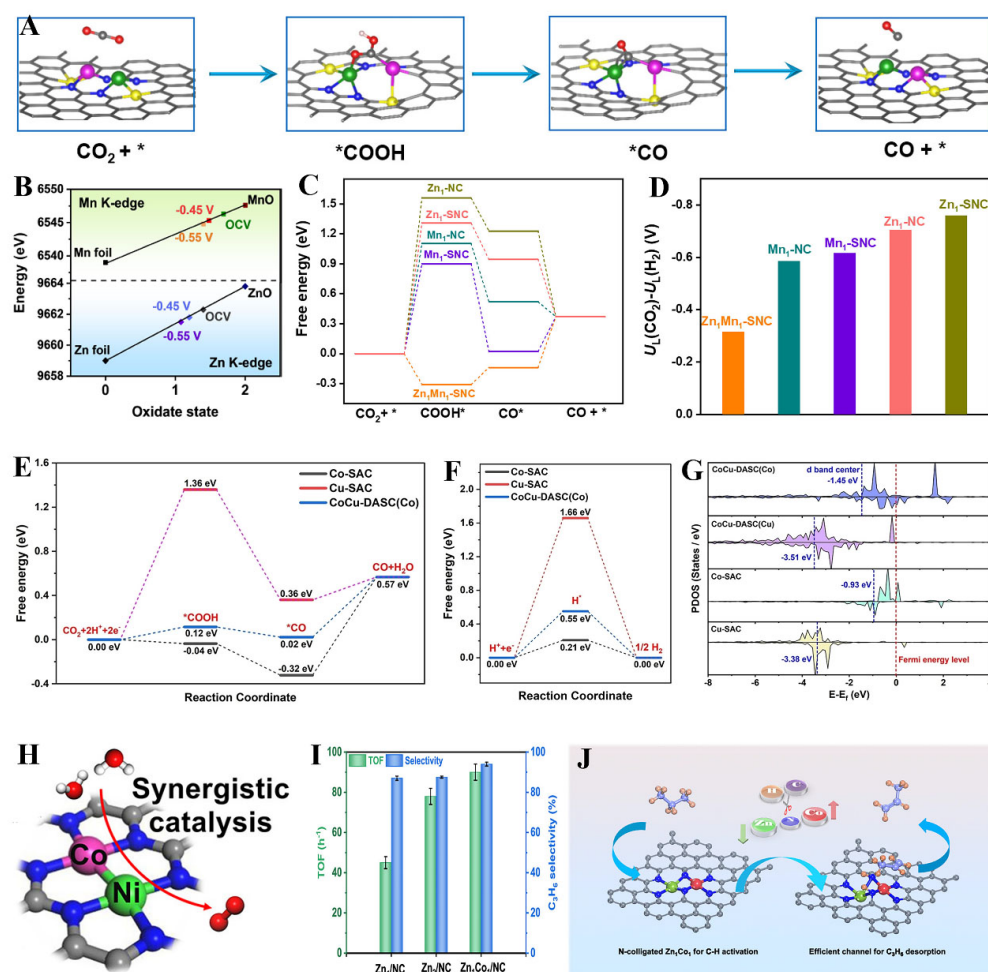


Figure 10. (A) Illustration of CO₂ reduction on Zn-Mn DAC; (B) *In situ* ATR infrared spectra; (C) Free-energy profiles for CO₂RR to CO; (D) The differences in limiting potential for CO₂RR and HER; (A-D) Reproduced with permission from Ref.^[159]. Copyright 2024, Wiley-VCH; (E) Free energy profiles of CO₂ reduction; (F) Free energy profiles of HER; (G) The pDOS for the CoCu-DASC, Co-SAC, and Cu-SAC; (E-G) Reproduced with permission from Ref.^[160]. Copyright 2022, Wiley-VCH; (H) Schematics of the NiCo synergy for OER. Reproduced with permission from Ref.^[163]. Copyright 2022, Wiley-VCH; (I) TOF values and C₃H₆ selectivity during PDH reaction on Zn₂/NC, Zn₂/NC, and Zn₂Co₂/NC; (J) Schematic diagram of the enhanced activation of C₃H₈ and selectivity of C₃H₆ for the PDH reaction; (I-J) Reproduced with permission from Ref.^[101]. Copyright 2024, American Chemical Society. DACs: Dual-atom catalysts; HER: hydrogen evolution reaction; SACs: single-atom catalysts; ATR: attenuated total reflection; OER: oxygen evolution reaction; TOF: turnover frequency; PDH: propane dehydrogenation.

industrial applications are still lacking, requiring more effort for precise design and investigation of the fundamental mechanism.

Except for the synergy of DACs in electrochemical CO₂ reduction, the cooperative role between dual-metal atoms makes it a promising candidate for the OER and ORR processes. Through strong metal-support interactions (SMSI) offered by nickel-vanadium layered double hydroxides (LDH), the significant interplay could anchor the Ru site to reach a fluctuation in oxidation state for cathodic HER, while the Ni site contributed to superior OER performance^[161]. Similarly, IrFe dual atoms with N₂Ir-N₂-FeN₂ configuration exhibited favorable bifunctional oxygen conversion. The Fe site facilitated the ORR, while the Ir site played a crucial role in the OER^[162]. Pei *et al.* designed atomically dispersed NiCo DAC towards OER^[163]. The synergistic interaction from the NiCo atomic pair optimized the electronic state and lowered the energy barrier; thus, the most favorable OER pathway was proposed [Figure 10H]. Additionally, ZnCu-NC DAC with atomic Cu-C₂N and Zn-N₄ sites was constructed by dynamic synthetic strategy^[164]. Importantly, the Zn

and Cu sites could effectively adsorb O_2 via the bridged-adsorption model, enhancing the orbital hybridization effect between metallic 3d and O 2p, thus improving ORR activity. Similarly, Zhao *et al.* found that the Fe-N₂-Fe structure could tune the adsorption configuration of O_2 and lower the cleavage barrier, thus accelerating the catalytic kinetics^[165]. Other than the intrinsic activity, structural and shape engineering of supports to expose more active sites are also of great importance in realizing excellent reactivity. A Fe-Mn dual atom anchored on an ultrathin 2D NC nanosheet was efficient for bifunctional ORR and OER^[98]. Moreover, Huang *et al.* also observed that Fe-Mn DAC with FeN₄-MnN₃ moiety exhibited superior ORR performance and almost suppressed the 2 e⁻ pathway^[166]. Recently, Pan *et al.* found that Pd₁Cu₁-TiO₂ DAC was more beneficial to urea production, where the synergy of Pd₁Cu₁ sites and oxygen vacancies played a critical role in promoting the direct C-N coupling^[167]. Apart from the electrochemical process, the synergy of dual-atom active centers in thermocatalysis was reported. Chai *et al.* developed a ZnCo-NC DAC as the main active site for the PDH^[101]. As shown in Figure 10I, ZnCo-NC DAC exhibited a higher turnover frequency (TOF) value of C₃H₈ conversion and enhanced C₃H₆ selectivity compared to Zn₁-NC and Zn₂-NC. Based on experimental and theoretical studies, a schematic illustration of the superior performance is depicted in Figure 10J. The N-bridged Zn and Co atoms promoted the scission of the C-H bond in C₃H₈. The steric effect of the dissociated H at the bridged N provided a feasible channel for C₃H₆ desorption. These results suggested that the role of the N-colligated ZnCo pairs was more crucial, with synergy for PDH.

In short, the cooperative effect of dual metal centers can largely enhance reactivity. The synergy is manifested in the following aspects. Firstly, compared to single atoms, the synergistic effect can break the restriction of scaling relations on activity. The adsorption-desorption behaviors of reactions can be optimized simultaneously on two different metal sites. Secondly, the DAC plays a bifunctional role in some reactions, such as when one metal is active for hydrogen production, and the other metal leads to superior performance for oxygen evolution. The dual-site bifunctional catalyst shows its great potential for practical application. Thirdly, the unique geometric configuration makes the structure diverse and flexible. The different configurations may result in different metal atomic distances, which determine the inter-metal interaction and adsorption behaviors of reactants. The specific configuration of DACs will influence the adsorption mode and strength of reactants, intermediates, and products, thus affecting the activity and selectivity. Particularly for the critical intermediates of C-C coupling, the synergy of dual metals can optimize adsorption configuration and promote the formation of C₂₊ products. Therefore, a universal macro-descriptor rigorously correlating the dual-atom configuration and intrinsic activity is critical to guide the design and preparation of advanced DACs. This opens a new avenue for future studies on DACs.

CONCLUSION AND OUTLOOK

DACs have been regarded as the new frontier in the field of energy conversion. In this review, we overview the recent progress in the controlled preparation of DACs. Then, the electronic structures and configurations of active centers are discussed. We focus on the microenvironment manipulation of active sites, including dual atoms with non-bonding interaction, N/O/S/Cl-bridged interaction, and direct metal bonding interaction. The merits in geometric and electronic configurations render the active moiety proper adsorption behavior towards intermediates. To better understand the structure-activity relationship and reaction mechanism, the catalytic role of DACs in the energy conversion application is clarified. Particularly, a fundamental understanding of the electronic effect and synergistic effect is demonstrated to guide the development of highly efficient DACs for practical applications.

So far, great progress has been achieved in DACs, but some important concerns and challenges are still worth considering and addressing.

Precise construction of uniform DACs

Current preparation approaches inevitably introduce single atoms, as well as a mixture of homonuclear and heteronuclear dual atoms. Developing new strategies to prepare uniform DACs is of great importance to establishing clear and definite structure-activity relationships.

From dual-center to multi-center design

DACs play a crucial role in bifunctional catalysts by the merits of dual metal centers. Except for DACs, some attention needs to be focused on the atomic clusters which include three or few atoms due to their unique structure and high efficiency. In addition, the well-regulated anchoring of diverse metal atoms into a single matrix shows good potential, such as high-entropy multi-atoms. This broadens the family of SACs and DACs, opening a new avenue for developing specific-atom catalysts with multi-centers.

In situ/operando characterization techniques

The characterizations of DACs are mainly by means of HAADF-STEM and X-ray adsorption spectroscopy. These techniques have difficulty differentiating the dual-metal atoms and identifying the specific metal species. In some situations, the scattering of small clusters is overlooked in the XAS analysis. Infrared spectroscopy with special probe molecules would be another powerful technique to provide additional structural information on dual atoms.

DACs library for universal design principles

Theoretical calculations not only aid in experimental design but also play a key role in elucidating the reaction mechanism. While traditional DFT calculations are usually performed, they are not feasible for high-throughput screening. The machine learning technique presents promise in the construction of predictive models. Pioneering works have already built up the library of databases. These remarkable examples offer a database for the next generation of highly efficient catalyst exploration with artificial intelligence.

Practical application in emerging fields of catalysis

Compared to classic thermocatalysis, electrocatalysis, and photocatalysis, plasms-catalysis and microwave-assisted catalysis remain at a nascent stage. The couple of multi-field catalysis of DACs is expected to be promising in the future. Another future direction is to bridge the gap between heterogeneous catalysis and bio-catalysis. Dual-metal centers are extensively present in metalloprotease. The structural similarity opens a new avenue for dual-atom structure regulation and their application in enzymatic and biomimetic catalysis.

DECLARATIONS

Authors' contributions

Prepared the manuscript: Chen, Y.

Revised the manuscript: Lin, J.

Availability of data and materials

Not applicable.

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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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