

Precise Synthesis of Dual-Atom Catalysts for Better Understanding the Enhanced Catalytic Performance and Synergistic Mechanism

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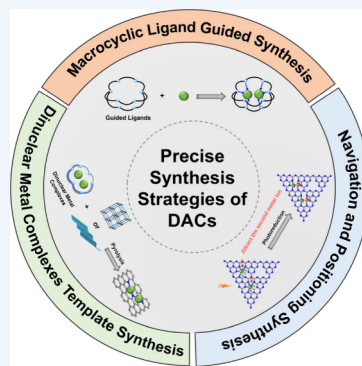
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CONSPECTUS: Dual-atom catalysts (DACs), featuring two catalytic sites in close proximity, have emerged as a new frontier in energy-related catalysis. Compared with single-atom catalysts (SACs), DACs have more space to optimize the catalytic performance by changing the dual-atom catalytic sites and their coordination environments. Through adjusting the compositions and coordination environments of the metal sites in DACs, it is possible to finely tune the electronic and geometric properties of active centers, and then the synergistic effects for facilitating substrates activation and intermediates stabilization can be strengthened or optimized, consequently tailoring diverse reaction pathways and achieving various challenging catalytic reactions. The most important yet challenging task in DACs studies is the precise synthesis of DACs, which is crucial to understand the relationship between the catalytic performance and structure at the atomic level. In most cases, DACs were synthesized via the pyrolysis of a mixture of metal salts and organic ligands, in which two metals are randomly distributed in DACs, and it was difficult to control the M...M distance (M = metal ion) and uniform dispersion of DACs. Hence, developing innovative strategies for the precise synthesis of DACs with definite structures and high-efficiency catalytic performance is urgently needed.

In this Account, we tentatively summarize the strategies for the precise synthesis of DACs and their applications in activation and conversion of small molecules such as H_2O , CO_2 , and so on. Focusing on the precise synthesis of DACs, three types of synthesis strategies have been put forward and systematically introduced. Based on the precise synthesis strategies, the applications of the resulting DACs with high purity in synergistically activating and converting small molecules have concurrently been discussed, including the cleavage of C–C bonds, activation and reduction of CO_2 and H_2O , and so on. Attempts have been made to explain why the catalytic performance of DACs for these functions is much higher than what SACs have achieved. Efforts have been made on revealing the influences of dual-metal site types, the separations between dual metals, their geometry configurations and coordination environments, as well as the ligand structures on the catalytic performance. Emphasis has been placed on the analysis of the structure–reactivity relationship and revealing the synergistic mechanism at the molecular level. Finally, perspectives on the current challenges and future development of DACs have been put forward. We anticipate and believe that this Account will provide profound insights into the synthesis of structurally defined DACs and give new insights of synergistic catalytic effects in DACs.



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- Ouyang, T.; Huang, H. H.; Wang, J. W.; Zhong, D. C.; Lu, T. B. A dinuclear cobalt cryptate as a homogeneous photocatalyst for highly selective and efficient visible-light-driven CO_2 reduction to CO in $\text{CH}_3\text{CN}/\text{H}_2\text{O}$ solution. *Angew. Chem. Int. Ed.* **2017**, 56, 738.² With the macrocyclic ligand guided synthesis strategy, a cobalt DAC was precisely synthesized, which displays a remarkably enhanced photocatalytic activity for CO_2

reduction. The concept of dinuclear metal synergistic catalysis (DMSC) was first proposed, and the synergistic mechanism was thoroughly investigated.

- Ouyang, T.; Wang, H. J.; Huang, H. H.; Wang, J. W.; Guo, S.; Liu, W. J.; Zhong, D. C.; Lu, T. B. Dinuclear metal synergistic catalysis boosts photochemical CO_2 -to-CO conversion. *Angew. Chem. Int. Ed.* **2018**, 57, 16480.³ Using the macrocyclic ligand guided synthesis strategy, a ZnCo heterometallic DAC with strengthened DMSC

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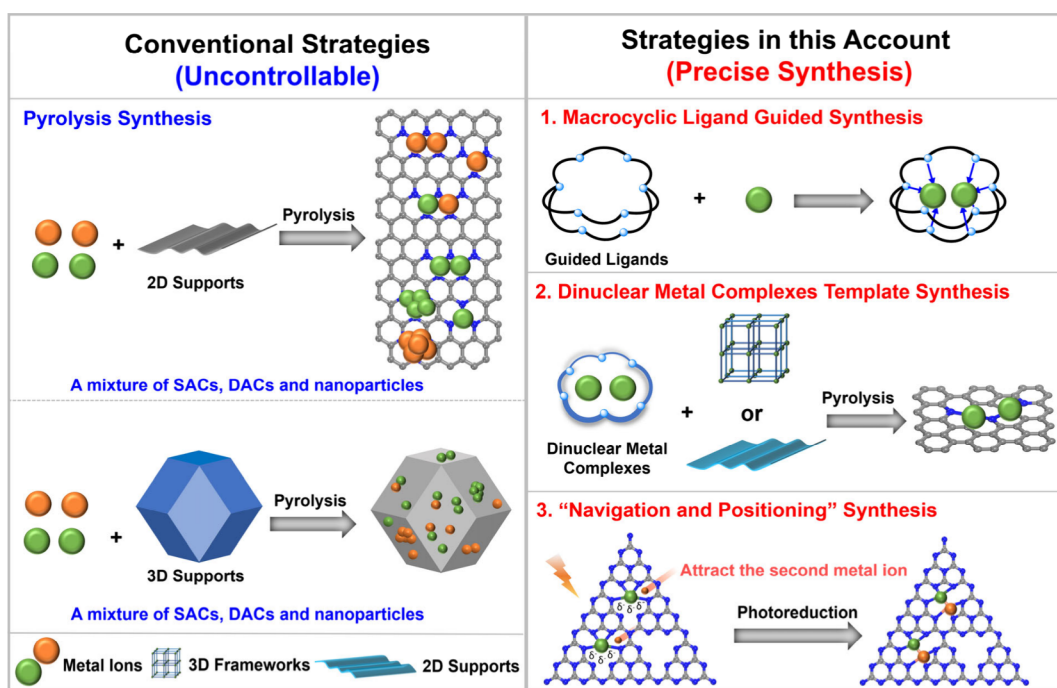


Figure 1. A comparison of the precise synthesis strategies of DACs presented in this Account with the conventional synthesis strategies of DACs.

effect and further enhanced photocatalytic activity for CO₂ reduction was rationally designed and synthesized.

- Gong, Y.-N.; Cao, C. Y.; Shi, W. J.; Zhang, J. H.; Deng, J. H.; Lu, T. B.; Zhong, D. C. Modulating the electronic structures of dual-atom catalysts via coordination environment engineering for boosting CO₂ electro-reduction. *Angew. Chem. Int. Ed.* **2022**, *61*, e202215187.⁴ Three dual Ni catalysts derived from a dinuclear Ni(II) complex were synthesized via a template synthesis strategy, where the relationship between electrocatalytic CO₂ reduction activity and coordination environments was revealed.
- Zhao, Q. P.; Shi, W. X.; Zhang, J.; Tian, Z. Y.; Zhang, Z. M.; Zhang, P.; Wang, Y.; Qiao, S. Z.; Lu, T. B. Photoinduced synthesis of heteronuclear dual-atom catalysts. *Nat. Synth.* **2024**, *3*, 497–506.⁵ A “navigation and positioning” strategy for the precise and scalable synthesis of a series of M₁M₂ (where M is a metal ion) heteronuclear dual-atom catalysts (DACs) was proposed, in which the photoinduced electron accumulation at the M₁ sites results in the capture and reduction of M₂ cations close to the M₁ sites to generate DACs with high purity.

1. INTRODUCTION

Catalysis is the backbone of the chemical industry. With the action of catalysts, many chemical products and medicines have been created by chemical synthesis, which greatly meets and enriches the life of humankind. Based on the number of catalytic centers, catalysts could be divided into single-atom catalysts (SACs), dual-atom catalysts (DACs), and multiatom catalysts (MACs). Since the pioneering work on SACs by Zhang et al. in 2011,⁶ the synthesis and applications of SACs have been extensively explored due to their maximal atomic utilization.^{7–11} However, it has been also found that the catalytic performances of SACs are limited in some catalytic

reactions that need the synergy of two or more catalytic sites. For these cases, SACs are a bit powerless at achieving such complex but meaningful catalytic reactions.

Faced with this dilemma, the introduction of a second catalytic site in the vicinity of the first one in a catalyst could be an effective strategy to overcome the limitations of SACs, by which DACs with unique electronic and geometric structures can be established. DACs may have more advantages in catalysis compared with SACs. (1) DACs can synergistically activate and convert small molecules, thus greatly boosting the catalytic activity. It has been evidenced that for small molecules such as CO₂ and H₂O conversion, DACs with dual-atomic catalytic sites show remarkably enhanced catalytic activity over the corresponding SACs.³ (2) DACs can achieve challenging catalytic reactions that SACs can not.¹² For some complicated catalytic reactions with multistep reaction processes, SACs may only accomplish one or two of the steps, while the whole reaction cannot proceed. In this case, DACs with two catalytic sites may have the potential to accomplish all the steps and achieve the reaction, as the two catalytic sites can assume different functions, which may promote the reaction by a cascade mode, thus meeting the reaction requirements. (3) DACs can serve as more ideal models to mimic biological enzymes,¹³ which is beneficial for the development of artificial mimetic enzymes. These advantages, together with those of high atom utilization efficiency and well-defined structures, enable DACs to have huge potential in current catalysis science. DACs have attracted much interest of researchers in the past and absolutely will attract more in the future.

During the past decades, we have been devoted to studying the precise synthesis of DACs and their applications in activation and conversion of small molecules such as CO₂ and H₂O. In this Account, combining with the pioneering works of DACs by others, we introduce our progress on the development of advanced synthetic tactics for precisely engineering DACs, as well as their catalytic performance. We begin with an overview of strategies for the precise synthesis of DACs that we

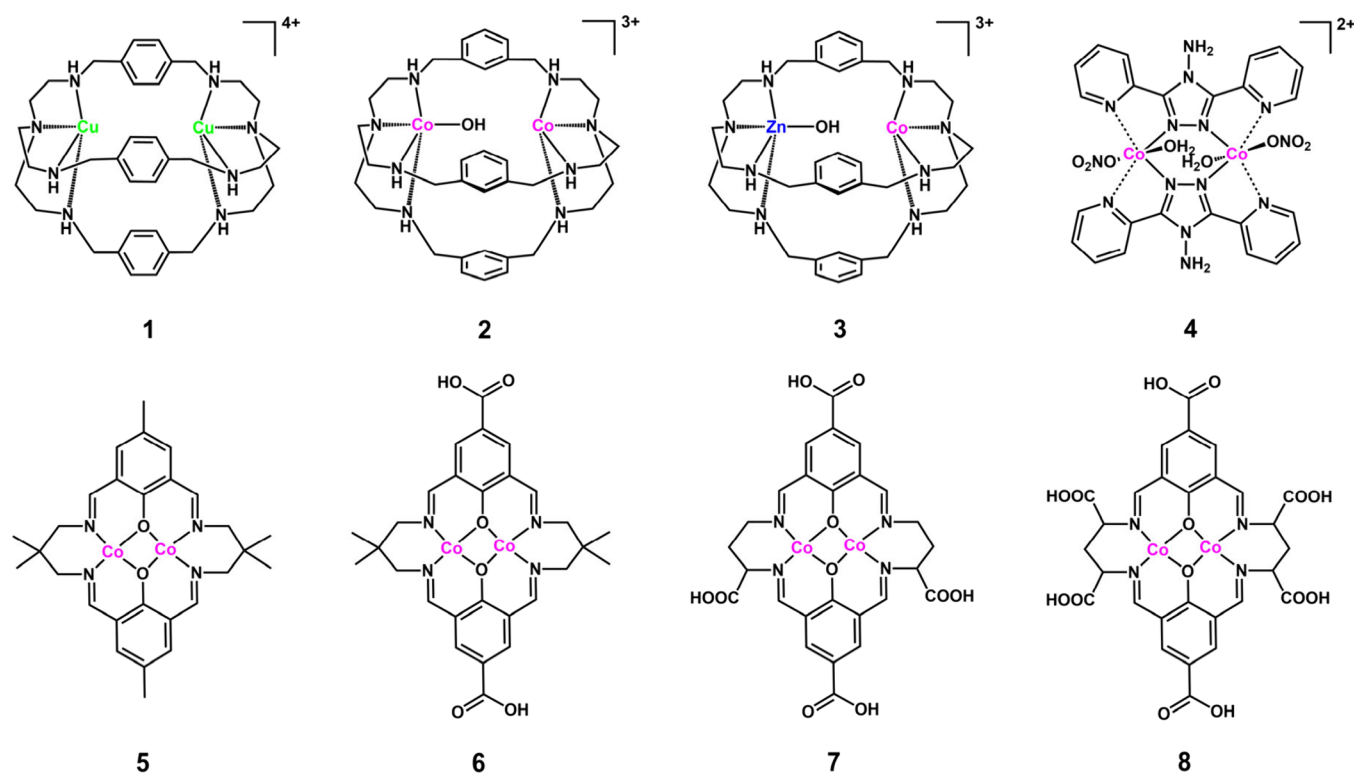


Figure 2. Representative structures of macrocyclic ligands and corresponding DACs.

have established, then highlight the broad applications of DACs in activation and catalytic conversion of small molecules. The first strategy is to design and synthesize distinctive macrocyclic ligands, in which specific dual metals are introduced to obtain dinuclear metal complexes with high purity and close metal–metal separations. The second is to adopt dinuclear metal complexes as precursors to synthesize DACs via a pyrolysis method, by which the main body structures of dinuclear metal sites can be preserved, and thus, DACs with homogeneously dispersed dual-atom sites can be facilely prepared. The third is the “navigation and positioning” strategy for the precise synthesis of heteronuclear DACs, in which the photogenerated electron accumulation at the first metal site on polymeric carbon nitride (PCN) can capture and reduce the second metal ion close to the former to generate heteronuclear DACs with high purity. Finally, we put forward the current challenges and developments of DACs in the future. This Account will give guidance for researchers to precisely synthesize DACs and puts forward new insights of synergistic catalytic effects in DACs.

2. SYNTHESIS STRATEGIES OF DACs

With two adjacent metal sites, DACs inherit the advantages of high atom utilization of SACs and also offer the capability to modulate the electronic structures of metal sites, thus improving the binding ability of metal sites with reactants.^{14,15} Obviously, it is undoubtedly true that the precise synthesis of DACs is crucial, which is beneficial for analyzing the structure–performance relationship at the atomic level and giving guidance for the rational design of efficient catalysts. Although several synthesis strategies of DACs such as conventional pyrolysis synthesis have been reported,^{16–19} the pyrolysis process is uncontrollable, and it usually gets a mixture of DACs with SACs and nanoparticles (Figure 1). The precise

synthesis of DACs with definite structures and homogeneously dispersed dual-atomic sites still remains a great challenge.

In the past two decades, we have performed a series of studies on the precise synthesis and catalysis applications of DACs.^{20–22} Our earliest work on DACs for the activation and transformation of small molecules was reported in 2004, where we found that a dinuclear copper(II) cryptate can activate and cleave the C–C bond of acetonitrile at room temperature.¹ Then, the synthesis strategies of DACs including macrocyclic ligand guided synthesis, dinuclear metal complexes template synthesis, as well as “navigation and positioning” synthesis were subsequently innovated (Figure 1). By these strategies, the pairing of dual-atom sites can be precisely manipulated, obtaining a series of DACs with well-defined structures for enhanced catalytic performance via dinuclear metal synergistic catalysis (DMSC) or dual-site synergistic catalysis.

2.1. Macrocyclic Ligand Guided Synthesis

A facile method for the synthesis of DACs is the design and synthesis of distinctive organic ligands with two separate binding sites, by which two metal sites can be introduced by coordination interactions and the confinement effect, to precisely synthesize dinuclear metal complexes with close metal–metal separation and suitable configuration (Figure 1). The synthesized DACs possess well-defined catalytic sites and maximized utilization of metal atoms, often showing enhanced catalytic performances over SACs for small molecule activation and conversion.^{23–28} In addition, their structure–performance relationship and catalytic mechanism are also easy to be studied. N-heterocyclic cryptands and Robson-type macrocyclic compounds are suitable organic ligands for constructing DACs (Figure 2), as these organic ligands possess multi-nitrogen atoms, which can usually form very stable dinuclear metal complexes via multiple chelation interaction between metal ions and multinitrogen atoms and thus can keep their

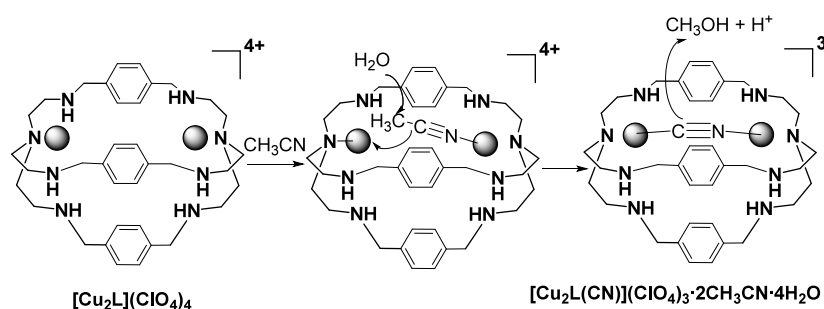


Figure 3. Possible mechanism for C–C bond cleavage of CH_3CN by $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$. Reproduced from ref 1. Copyright 2004 American Chemical Society.

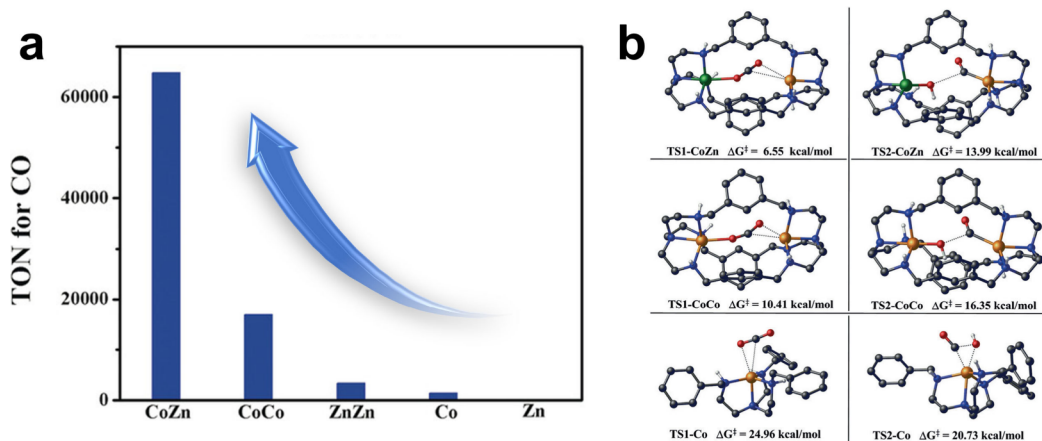


Figure 4. (a) The photocatalytic activity of CoZn, CoCo, ZnZn, Co, and Zn. (b) The energy barriers of two transition states for CoZn, CoCo, and Co in CO_2 -to-CO reduction reaction (Co, orange; Zn, green; C, gray; N, blue; O, red). Adapted with permission from refs 2 and 3. Copyright 2017 Wiley-VCH and Copyright 2018 Wiley-VCH.

dinuclear structure during long-term catalytic processes. N-heterocyclic cryptands could be structurally regarded as small cage molecules formed by connecting two tripodal organic groups together. The coordination interactions of N atoms and the confinement of the cage endow the cryptand ligands prone to combine with two metal ions to form a dinuclear metal complex. By tuning the metal–metal separations, the synergistic catalysis effect can be adjusted. In addition, by changing the metal species, homo/heteronuclear bimetal complexes can be synthesized, which can show diverse catalysis activity. Robson-type macrocyclic compounds are approximately planar organic ligands, with which the formation of dinuclear metal complexes is also based on coordination interactions and confinements. The resulting dinuclear metal complexes display planar structures, in which the metal species can be tuned on purpose, but their metal–metal distances are fixed in about 3.1 Å. Moreover, the π -conjugated systems in their structures can enhance charge transport and modulate the electric properties of metal centers, which can further promote the catalytic efficiency.

Since the first N-heterocyclic cryptand synthesized by Lehn et al. in the 1970s,²⁹ much effort has been devoted to developing macrocyclic ligands with diverse functions. In 2004, we synthesized a dinuclear Cu(II) N-heterocyclic cryptate of $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$ by the reaction of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and L^1 in methanol (Figure 2, complex 1).¹ The successful synthesis of $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$ was confirmed by single-crystal X-ray diffraction and electrospray ionization mass spectrometry (ESI-MS) measurement. Interestingly, when $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$

was dissolved in acetonitrile and stood at room temperature, $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$ showed an interesting activation and cleavage of the C–C bond of CH_3CN , resulting in a stable cyanide-bridged dinuclear Cu(II) complex $[\text{Cu}_2\text{L}^1(\text{CN})](\text{ClO}_4)_3$. The reaction mechanism involving a unique interaction between Cu(II) and CH_3CN was revealed in our subsequent work.³⁰ The chiral nitrile (*S*)-(+)-2-methylbutyronitrile was employed to react with $[\text{Cu}_2\text{L}^1](\text{ClO}_4)_4$. The results demonstrated that the N atom of CH_3CN first binds to one Cu(II) in $[\text{Cu}_2\text{L}^1]^{4+}$, and the other Cu(II) likely interacts with the filled π -orbital of the sp -hybridized C atom of CH_3CN . This interaction leads to electron flow from the π -bond to the Cu^{II} atom, increasing the “leaving ability” of the cyanide and enhancing the electrophilicity of the alkyl C atom. Consequently, the C–C bond undergoes cleavage via an $\text{S}_{\text{N}}2$ -type mechanism in the presence of adventitious water, forming (*R*)-(-)-2-butanol with opposite chirality and a $[\text{CuL}^1(\text{CN})]^{3+}$ complex (Figure 3).

We further synthesized a dinuclear Co(II) complex of $[\text{Co}_2(\text{OH})\text{L}^2](\text{ClO}_4)_3$ on the basis of a similar N-heterocyclic cryptand ligand by the reaction of $\text{Co}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ with L^2 under an Ar atmosphere (Figure 2, complex 2).² With the coordination interactions and confinement effect of L^2 , two Co(II) are restricted in the cavity of L^2 with a $\text{Co} \cdots \text{Co}$ distance of ~ 5.8 Å. We found that $[\text{Co}_2(\text{OH})\text{L}^2](\text{ClO}_4)_3$ has strong binding to CO_2 in acetonitrile. Exposed in air for less than 30 s, a carbonate-bridged complex of $[\text{Co}_2\text{L}^2(\mu\text{-O}_2\text{CO})](\text{ClO}_4)_2$ was formed.³¹ This observation indicates that $[\text{Co}_2(\text{OH})\text{L}^2](\text{ClO}_4)_3$ may show great potential in CO_2 reduction. Photocatalytic experiments showed that this complex really

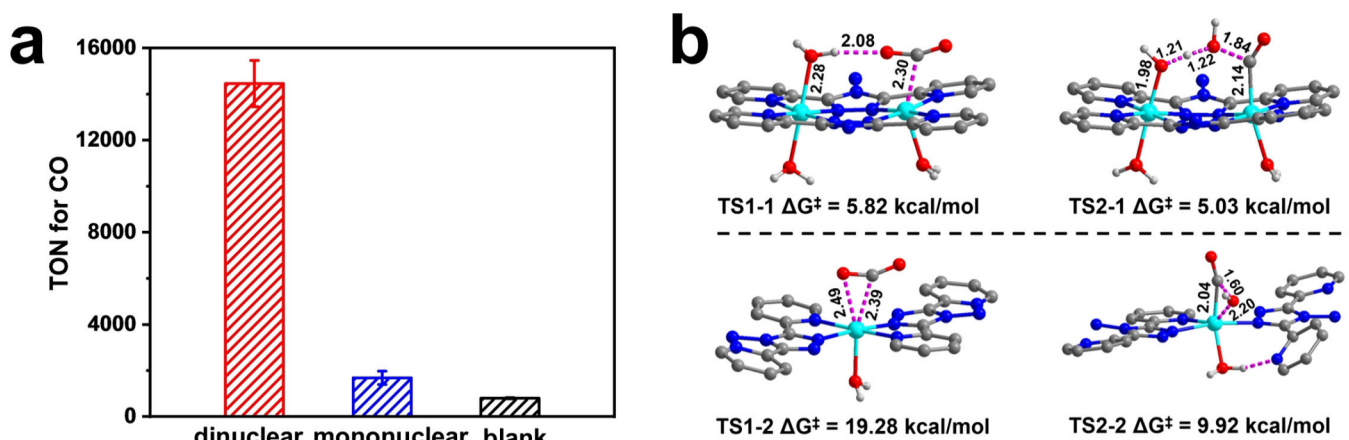


Figure 5. (a) TON values of dinuclear and mononuclear Co(II) complexes for photocatalytic CO₂ reduction to CO. (b) The energy barriers of two transition states in CO₂ reduction to CO for dinuclear and mononuclear Co(II) complexes with planar configuration, where the numerical values labeled on the structures represent the corresponding bond length (Å). Adapted with permission from ref 24. Copyright 2024 Wiley-VCH.

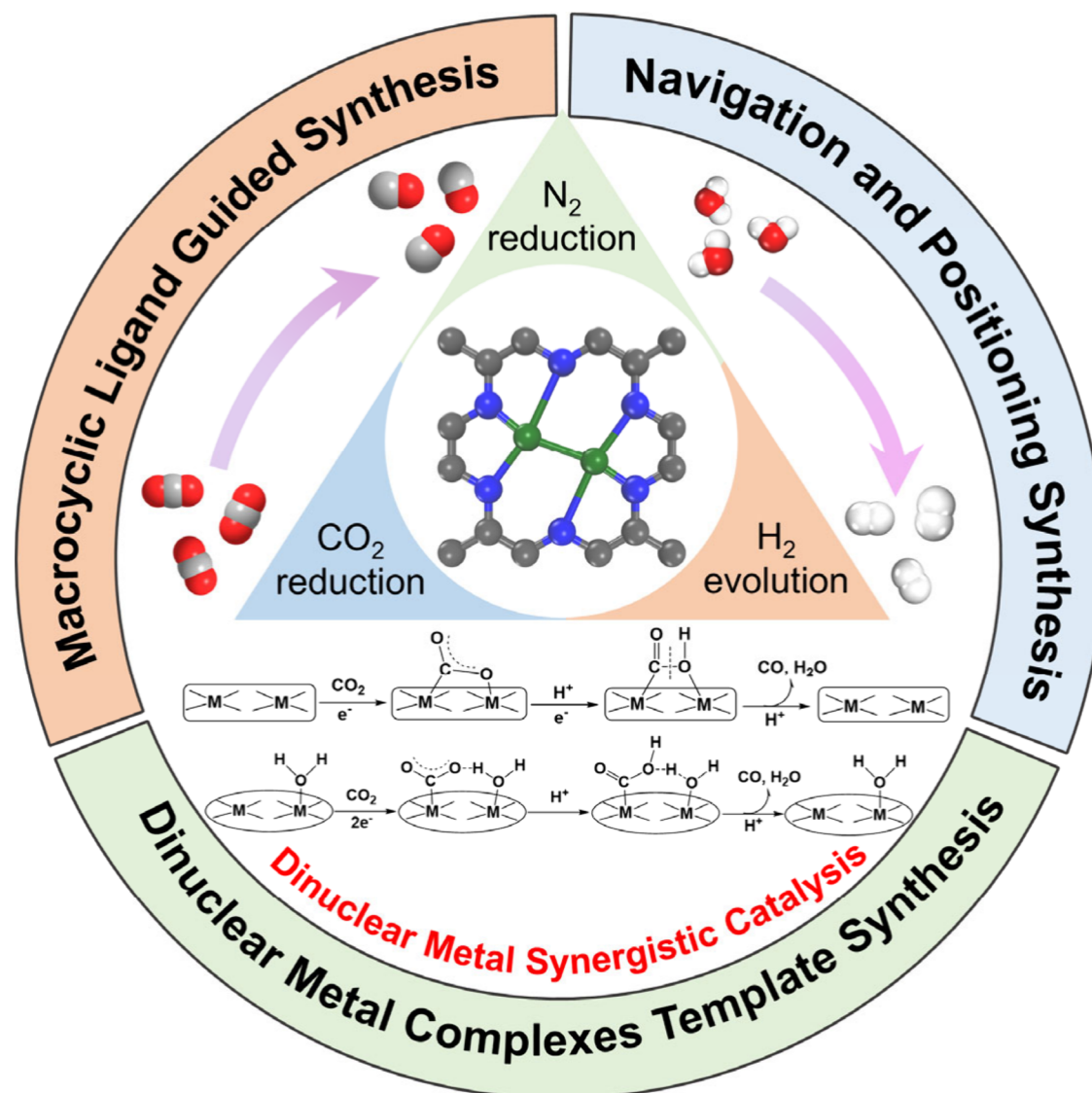
displays exceptionally high photocatalytic activity for the conversion of CO₂ to CO, achieving a turnover number (TON) of 16 896 and a turnover frequency (TOF) of 0.47 s⁻¹. These values significantly surpass those of the related mononuclear Co(II) complex (Figure 4a) and the most reported dinuclear complexes. The superior catalytic activity of [Co₂(OH)L²](ClO₄)₃ can be attributed to the dinuclear metal synergistic catalysis (DMSC) effect between two Co(II) ions, where one Co(II) acts as the primary catalytic site for CO₂ binding and reduction, while the other serves as an auxiliary catalytic site facilitating the cleavage of the C–OH bond in the [O=C–OH][‡] intermediate and subsequent removal of the –OH group. The more readily the C–OH bond is eliminated, the faster the conversion of CO₂ to CO occurs. Density functional theory (DFT) calculations reveal that the C–OH bond cleavage in the [O=C–OH][‡] intermediate is the rate-determining step (RDS) for the whole CO₂ reduction reaction. For [Co₂(OH)L²](ClO₄)₃, the DMSC effect between two Co(II) promotes the C–OH bond cleavage in the [O=C–OH][‡] intermediate, thus exhibiting a substantially lower energy barrier than its mononuclear counterpart (Figure 4b). Based on the above catalytic mechanism, considering the stronger affinity of Zn(II) to the –OH group than that of Co(II), we speculated the DMSC effect between Co(II) and Zn(II) would be stronger than that between Co(II) and Co(II), and the photocatalytic activity of CoZn heterodinuclear complex may further enhanced. Therefore, we rationally designed and synthesized a heterodinuclear CoZn complex of [CoZn(OH)L²](ClO₄)₃ (Figure 2, complex 3).³ As anticipated, [CoZn(OH)L²](ClO₄)₃ exhibited a much enhanced photocatalytic activity for CO₂ reduction to CO, with a TON of 65 000 and a TOF of 1.8 s⁻¹, 4-fold and 19-fold higher than those of the homodinuclear Co(II) and Zn(II) complexes. DFT calculations indicate that the DMSC effect between Co(II) and Zn(II) is really strengthened compared with that between Co(II) and Co(II) as well as that between Zn(II) and Zn(II). The strengthened DMSC effect significantly reduces the energy barrier of the rate-determining step of the CO₂-to-CO reduction reaction, leading to a substantial increase in photocatalytic activity for CO₂ reduction.

Inspired by the above results, we further designed and synthesized a dinuclear Co(II) complex of [Co₂(μ-OH)(BPMAN)](ClO₄)₃ containing an –OH group (BPMAN =

2,7-[bis(2-pyridyl-methyl)aminomethyl]-1,8-naphthyridine). It is well-known that –OH groups are extensively observed in natural enzymes, which play important roles in enzyme catalysis. In [Co₂(μ-OH)(BPMAN)](ClO₄)₃, the N atoms in BPMAN are capable of coordinating with two Co(II) ions, with a Co⋯Co distance of 3.3 Å. This catalyst not only exhibits DMSC for CO₂ photoreduction but also possesses an excellent capture capacity to CO₂ due to the existence of the –OH group. As a result, this dinuclear Co(II) complex exhibits a much high photocatalytic activity for CO₂ reduction to CO.³² Additionally, a mononuclear Ni complex featuring a S₂N₂-tetradentate ligand was synthesized for photocatalytic CO₂ reduction, which includes two uncoordinated pyridine pendants. These pendants can capture a Mg²⁺ ion as a Lewis-acid cocatalytic site, leading to the generation of a synergistic catalysis effect for the photocatalytic CO₂ reduction to CO.³³ Beside CO, HCOO⁻ can also be produced in photocatalytic CO₂ reduction by dinuclear metal complexes. Robert et al. synthesized a dinuclear Co(II) complex bearing a bi-quaterpyridine ligand, which can selectively photocatalyze CO₂ reduction into HCOO⁻ or CO via DMSC between two Co(II) sites, and the selectivity can be steered toward HCOO⁻ or CO simply by changing the acid cosubstrate.³⁴

In addition to N-heterocyclic cryptands, we also designed and synthesized a series of planar multinitrogen organic ligands for constructing dinuclear metal complexes. Utilizing the ligand guided synthesis strategy, we obtained a dinuclear Co(II) complex of [Co₂(L³)₂(H₂O)₂(NO₃)₂](NO₃)₂ (Figure 2, complex 4).²⁴ Each Co(II) ion is six-coordinated with four N atoms of two L³ ligands in the basal plane and two O atoms from one H₂O and one NO₃⁻ at the axial positions. Two L³ bridge two Co(II) ions with a Co⋯Co distance of 4.163 Å. Notably, this dinuclear Co(II) complex exhibits significantly elevated photocatalytic activity for CO₂ reduction to CO, with a TON of 14 457 and a TOF of 0.40 s⁻¹, much higher than those of the corresponding mononuclear Co(II) complex (Figure 5a). Control experiments and theoretical calculations have demonstrated that the superior catalytic activity of the dinuclear Co(II) complex is attributed to the indirect DMSC effect between two Co(II) ions. That is, one Co(II) binds one CO₂ molecule, and the other coordinates with one H₂O molecule, which is able to not only stabilize the adsorbed CO₂ molecule by an intramolecular hydrogen bond but also provide

Scheme 1. The Main Contents of This Account, with Direct (Top) and Indirect (Bottom) Synergistic Catalytic Pathways



a proton to promote the cleavage of the C–O bond in the $[\text{O}=\text{C}-\text{OH}]^\ddagger$ intermediate. Additionally, the energetically feasible one-step two-electron transfer process by the $\text{Co}_2^{\text{I,II}}$ intermediate to afford the $\text{Co}_2^{\text{II,II}}(\text{CO}_2^{2-})$ intermediate and the fast mass transfer closely related with the catalyst planar structure also contribute to the enhancement of the photocatalytic CO_2 reduction activity (Figure 5b).

Robson-type compounds are also a type of organic ligand benefiting from coordination interactions and the confinement effect to immobilize two metal ions to construct dinuclear metal complexes. Very recently, we have designed a series of dinuclear $\text{Co}(\text{II})$ complexes based on Robson-type ligands with different numbers of $-\text{COOH}$ groups through the macrocyclic ligand guided synthesis strategy (Figure 2, complexes 5–8).²³ The results of photocatalytic CO_2 reduction experiments show that all these dinuclear $\text{Co}(\text{II})$ complexes possess photocatalytic activity for CO_2 reduction, producing a large amount of CO and a trace amount of H_2 . With the increase of the number of $-\text{COOH}$ groups in dinuclear $\text{Co}(\text{II})$ complexes, the amount of CO generated markedly increases. The results of control experiments and DFT calculations show that the kinetics of CO_2 reduction

reactions are highly dependent on the rate of electron and proton transfer to the reaction intermediates adsorbed at the catalytic sites. The activation energy of the RDS in CO_2 reduction to CO via intramolecular proton transfer ($\Delta G^\ddagger = 8.09$ kcal/mol) is much lower than that via intermolecular proton transfer ($\Delta G^\ddagger = 16.99$ kcal/mol), indicating that an intramolecular proton transfer pathway is more favorable for CO_2 reduction to CO. More carboxylic groups in a dinuclear catalyst endow the catalyst with more proton relays, thus accelerating the proton transfer and boosting the photocatalytic CO_2 reduction.

Besides homogeneous catalytic systems, the observed DMSC effect in dinuclear metal complexes can also be introduced into heterogeneous catalytic systems, which not only boosts the catalytic activity but also improves the recyclability and reuse of catalysts, aiming at practical applications. For instance, by heterogenization of the dinuclear $\text{Co}(\text{II})$ complex of $[\text{Co}_2(\text{OH})\text{L}^2](\text{ClO}_4)_3$ via a covalent linkage, we successfully synthesized two new porous polymers of $\text{Co}_2\text{-P1}$ and $\text{Co}_2\text{-P2}$, which exhibited ultrahigh catalytic activity for photochemical CO_2 -to-CO conversion due to the existence of the DMSC effect between two Co sites.³⁵ Besides,

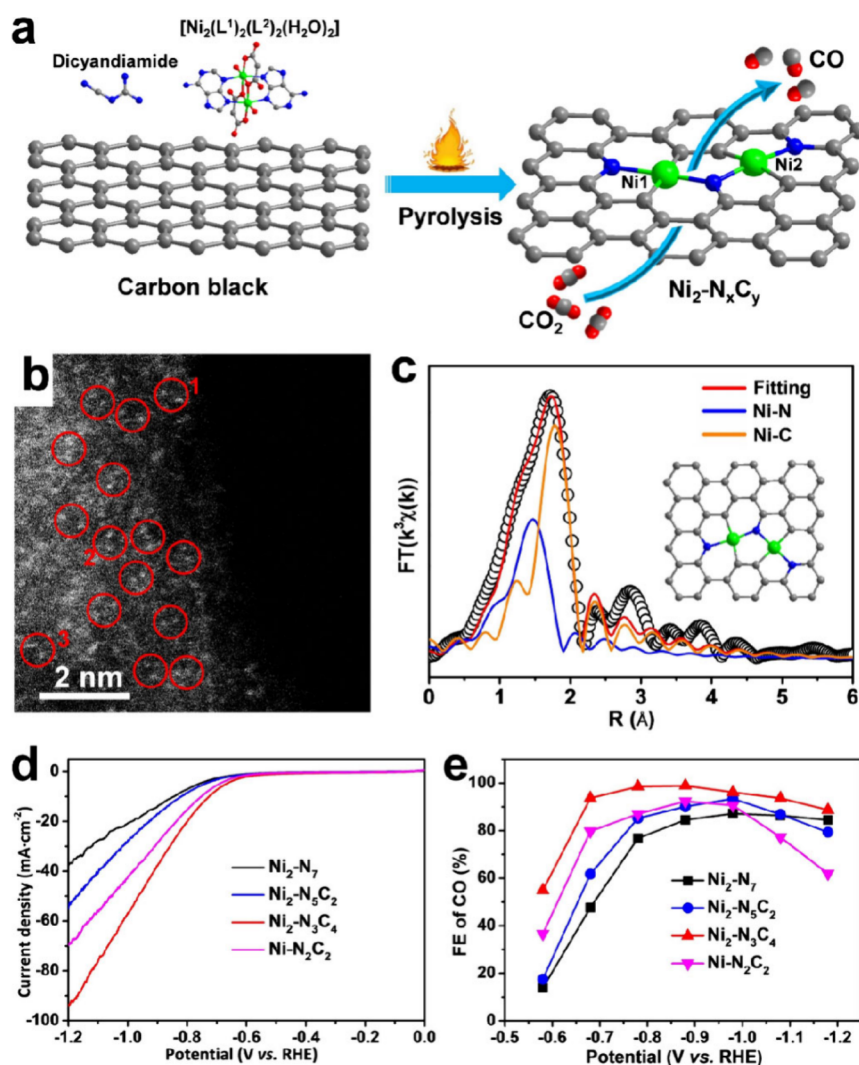


Figure 6. (a) Illustration showing the fabrication of $\text{Ni}_2\text{-N}_x\text{C}_y$ catalysts by template synthesis strategy for electrocatalytic CO_2 reduction to CO. (b) Magnified high-angle annular dark-field scanning transmission electron microscopy image of $\text{Ni}_2\text{-N}_3\text{C}_4$, showing dual Ni_2 sites highlighted by red circles. (c) EXAFS fittings and optimized models for $\text{Ni}_2\text{-N}_3\text{C}_4$ (inset). (d) LSV curves and (e) FEs for CO of $\text{Ni}_2\text{-N}_x\text{C}_y$ and $\text{Ni-N}_2\text{C}_2$ at different applied potentials. Adapted with permission from ref 4. Copyright 2022 Wiley-VCH.

we also developed a series of efficient catalysts of metal–organic frameworks (MOFs) and hydrogen-bonded organic frameworks (HOFs) containing dual-metal catalytic sites for synergistically boosting CO_2 reduction and hydrogen evolution reaction (HER).^{36–39} To endow dinuclear metal complexes with more functions, we also composited them with semiconductors through electrostatic^{40–43} or coordination interactions⁴⁴ to obtain a series of composite photocatalysts with photosensitivity, photoreduction, and photooxidation functions.

In addition to CO_2 reduction and HER, dinuclear metal complexes have also shown catalytic activity for N_2 reduction. It has been found that DACs not only enable the efficient adsorption of N_2 in a stable side-bridge mode but also facilitate the activation and conversion of N_2 by modulating the geometric and electronic structures of active sites.⁴⁵ For example, Schneider et al. synthesized a dinuclear rhenium complex featuring a N_2 -bridged structure. With the help of visible light, this complex demonstrated remarkable catalytic performance in the transformation of N_2 with benzoyl chloride

to benzamide and benzonitrile, achieving an overall yield of 61%.⁴⁶

The above discussion has clearly demonstrated that the design and selection of organic ligands are crucial for the synthesis of dinuclear metal complexes, which significantly influence their stability and catalytic activities. In N-heterocyclic cryptands, the two tris(2-aminoethyl)amine units linked by three phenyl groups can encapsulate two metal ions within its cage to form stable DACs, with metal–metal separations of 5.8 Å. Such separation allows two metal sites to bind to the $^*\text{COOH}$ intermediate simultaneously, which can dramatically weaken and activate the C–OH bond of $^*\text{COOH}$ through a direct synergistic catalytic pathway (Scheme 1), thus significantly reducing the energy barrier of the CO_2 -to-CO reduction reaction and leading to a substantial increase in photocatalytic activity compared to that of corresponding SACs. Replacing one Co in $[\text{Co}_2(\text{OH})\text{L}^2]^+$ (complex 2) with Zn produces $[\text{CoZn}(\text{OH})\text{L}^2]^+$ (complex 3); 3 exhibits a more enhanced photocatalytic activity for CO_2 reduction to CO than 2 due to the stronger Zn–OH interaction with the $^*\text{COOH}$ intermediate. When the metal–metal separations are shortened

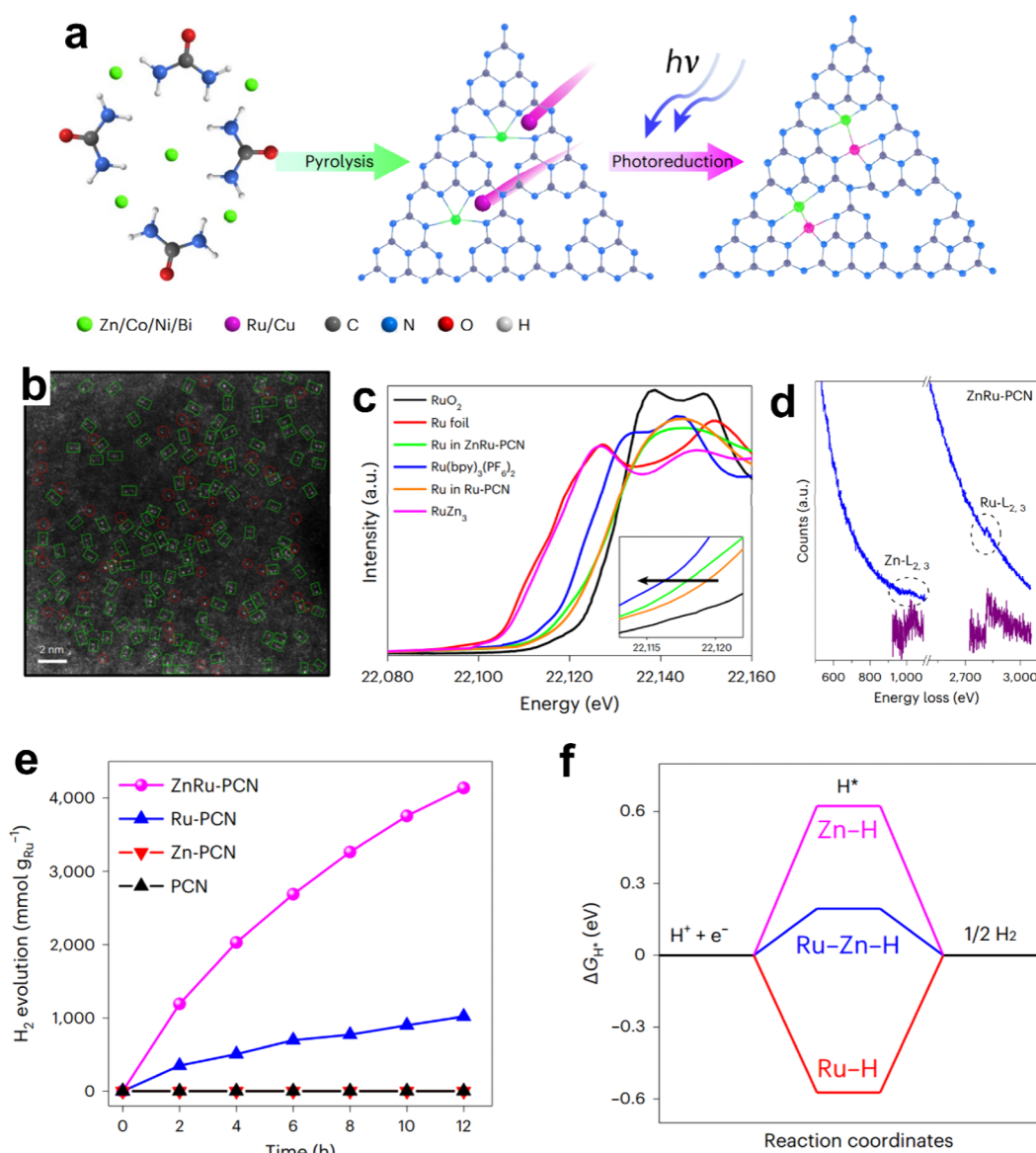


Figure 7. (a) Schematic illustration of the "navigation and positioning" strategy for fabricating heteronuclear DACs. (b) HAADF-STEM image of ZnRu-PCN. (c) Ru K-edge XANES. The inset is a partial enlargement of (c). (d) EELS for ZnRu-PCN. (e) H₂ production of ZnRu-PCN and referred samples. (f) Gibbs free energy change (ΔG_{H^*}) for hydrogen evolution on Zn-PCN, Ru-PCN, and ZnRu-PCN catalysts. Adapted with permission from ref 5. Copyright 2024 Nature Publishing Group.

to 4.1 Å in complex 4, and 3.1 Å in complexes 5–8, such short distances cannot allow the *COOH intermediate to insert into the space of two metal sites; thus, an indirect synergistic catalytic pathway (Scheme 1) is employed by two metal sites, where one metal site binds a CO₂ molecule and the other coordinates with a H₂O molecule. The coordinated H₂O is able to not only stabilize the adsorbed CO₂ molecule via hydrogen bonding but also provide protons to promote the cleavage of the C–OH bond in the [O=C–OH][‡] intermediate, boosting the activation and conversion of CO₂. In all, the precise synthesis of DACs can be readily achieved by the ligand directed synthesis strategy, where the key is the delicate design and successful synthesis of desired organic ligands.

2.2. Dinuclear Metal Complexes Template Synthesis

High-temperature pyrolysis is the most common method for preparing atomically dispersed catalysts, including SACs,

DACs, and so on.^{47–50} A number of SACs have been synthesized by the pyrolysis of metal salts, mononuclear metal complexes, MOFs, or MOF nanosheets, where the metal sites in the precursor matrix can be transferred and anchored on the supports.^{51–54} In contrast, the precise synthesis of DACs by the conventional pyrolysis method is slightly complicated and difficult, as the resulting catalysts usually contain a mixture of SACs, DACs, and nanoparticles and the M···M distances in DACs are also hardly controlled. Dinuclear metal complexes template synthesis is defined as using dinuclear metal complexes as precursors, which are first adsorbed on the 2D materials or confined in 3D porous materials and then pyrolyzed at certain temperatures. Different from the conventional pyrolysis method, in dinuclear metal template synthesis, the coordination and confinement of organic ligands can prevent dual-metal site migration and aggregation; thus, it has more opportunity to obtain DACs with dual-atom pairs homogeneously dispersed. Obviously, the

design and selection of dinuclear metal complex precursors are important, where the distances between two metal centers should be considered. The high thermal stability of dinuclear metal complexes is also necessary to make sure the main body structures of dual-metal sites are preserved during pyrolysis processes. In addition, the pyrolysis conditions such as the temperature, atmosphere, etc., also need to be optimized for the precise synthesis of DACs via dinuclear metal complexes template synthesis.

Recently, we and others used the dinuclear metal complexes template synthesis strategy for the precise synthesis of DACs,^{4,21,55–58} in which the coordination bonds between the metal sites and organic ligand in dinuclear metal complexes can really effectively stabilize the dual-metal pair, thus preventing the aggregation of metal atoms during the pyrolysis process, which enables the precise and controllable synthesis of DACs. Further adjusting the local coordination environments of the metal sites, the catalytic performance can be optimized.

In 2022, we carried out the pyrolysis of a dinuclear Ni(II) complex with carbon black and dicyandiamide at 700, 800, and 900 °C, respectively, affording three Ni-based DACs (Ni₂-N₇, Ni₂-N₅C₂, and Ni₂-N₃C₄) with slightly different coordination environments around the dual-atom Ni₂ sites (Figure 6a).⁴ The high-angle annular dark-field scanning transmission electron microscopy (HAADF-STEM) images clearly show paired bright dots with a distance of ~3.1 Å, corresponding to dual Ni₂ atoms (Figure 6b). The Fourier transformation extended X-ray fine structure (FT-EXAFS) spectra and X-ray photoelectron spectroscopy (XPS) spectra demonstrate that there are both Ni–N and Ni–C bonds in Ni₂-N₅C₂, Ni₂-N₃C₄, and Ni-N₂C₂, while there are only Ni–N bonds in Ni₂-N₇ (Figure 6c). Ni₂-N₃C₄ displays the best electrocatalytic activity for CO₂ reduction, with the highest CO Faradaic efficiency of 98.9% (Figure 6d,e). DFT calculations demonstrate that regulating the coordination environments can modulate the electronic structures around the Ni sites, which improves the binding energies to *COOH and *CO intermediates. For Ni₂-N₃C₄, the proper binding energies of Ni sites to *COOH and *CO facilitate the formation of *COOH and the release of *CO, resulting in a minimal reaction free energy and the best catalytic performance. In the same way, we used another dinuclear Ni complex as a precursor to pyrolyze with carbon nanotubes and dicyandiamide in Ar, obtaining a DAC of Ni₂-NCNT (NCNT = N-doped carbon nanotube). High-resolution transmission electron microscopy (HRTEM) and scanning electron microscopy (SEM) images reveal that Ni₂-NCNT inherited the morphology of CNTs, with a purity of Ni₂ DACs of 90.1%.⁵⁷ Ni₂-NCNT exhibits superior activity and selectivity for electrocatalytic CO₂ reduction to CO, with a partial current density for CO (*j*_{CO}) of 76 mA cm^{–2} and a Faradaic efficiency of 97%. The *j*_{CO} mass activity of Ni₂-NCNT is 2.3 times higher than that of the corresponding Ni₁-NCNT. DFT calculations reveal that the synergistic catalysis between two Ni atoms contributes to lowering the reaction free energy for *COOH formation, thus greatly boosting the electrocatalytic CO₂ reduction. Besides dinuclear metal complexes, MOFs were also used as templates for the synthesis of DACs by pyrolysis, where the first is the introduction of one or two metals into the pores of MOFs. The subsequent pyrolysis of treated MOFs can fabricate DACs.^{59–63}

2.3. “Navigation and Positioning” Synthesis

As discussed above, high-temperature pyrolysis still faces challenges for the control of purity and M···M distance during the synthesis of DACs. We recently developed a unique “navigation and positioning” strategy for the precise and scalable synthesis of a series of heteronuclear DACs of ZnRu-, NiRu-, ZnCu-, CoCu-, NiCu-, and BiCu-PCN on a polymeric carbon nitride (PCN) support (Figure 7a). This strategy involves two steps of pyrolysis and light irradiation processes. First, M₁-PCN SACs were synthesized by directly calcining urea and metal salts. Upon photoexcitation, negative charge accumulation occurs at the M₁ nucleation site in M₁-PCN, which can attach the secondary metal ion of M₂ around the M₁ site, generating a series of heteronuclear DACs of M₁M₂-PCN with over 80% purity.⁵ For ZnRu-PCN DACs, HAADF-STEM images indicate the homogeneous dispersion of Ru and Ni atoms on the PCN support (Figure 7b). The absorption edge energy of Ru K-edge XANES confirms the Ru oxidation state is between +2 and +4 (Figure 7c). Atomic resolved electron energy-loss spectroscopy further substantiates the presence of Ru and Ni atoms within the dual-atom sites (Figure 7d). Among these obtained heteronuclear DACs, ZnRu-PCN shows extraordinary catalytic activity toward the photocatalytic hydrogen evolution reaction, with a H₂ evolution of 4138 mmol/g_{Ru} in 12 h, four times higher than that of Ru-PCN (Figure 7e). DFT calculations indicate the synergistic effect between the Ru–Zn atoms. As shown in Figure 7f, the Δ*G*_{H*} value for Ru–Zn–H was 0.195 eV, which is favorable for the HER process. This strategy underlines a promising and universal approach for the precise synthesis of highly purified DACs by a simple photoinduced charge accumulation and navigation process, which has been employed to precisely synthesize DACs by other researchers. For example, Zhu et al. used this strategy for the precise synthesis of PtCo DAC on CN for photocatalytic hydrogen evolution, in which the Co-SAC was initially anchored on the CN support, and photoinduced electron accumulation at the Co sites resulted in the capture and reduction of Pt metal ions near the Co sites to obtain PtCo DAC with high purity.⁶⁴

3. CONCLUSION AND OUTLOOK

In this Account, we have discussed the precise synthesis strategies of DACs and their advancements in energy conversion from a molecular perspective. It has been observed that DACs possess more advantages over SACs in the activation and transformation of small molecules owing to the existence of the DMSC effect, which endows them with higher catalytic activity and product selectivity than SACs. With the well-defined structures of DACs, it is beneficial to explore the activity–structure relationship. Despite the remarkable progress that has been made in the synthesis and applications of DACs, the following key challenges should be further considered and addressed.

First, the design of ligand architecture is of great importance for precise syntheses of DACs based on dinuclear metal complexes, as it guides the formation of dinuclear metal complexes. With the rational combination of metals and directing ligands, dinuclear metal complexes with suitable M···M distances and enhanced catalytic activity are expected to be precisely synthesized. However, the influence of metal species and M···M distance in DACs on the catalytic activity and production selectivity has not been thoroughly investigated, as

the DMSC effect of DACs is close related to the M...M distance in DACs. Moreover, the synthesis of heterometallic dinuclear complexes is still a great challenge. In addition, though dinuclear metal complexes template synthesis is a simple and effective approach for the precise synthesis of DACs, the precise synthesis of highly loaded DACs remains a significant challenge, as SACs and clusters often coexist with DACs. To address this issue, it is essential to meticulously control the conditions in pyrolysis, including the reaction temperature, the ratio of dinuclear metal complex and support, and so on, aiming at preventing the metals from aggregating.

Second, the determination of definite structures of dinuclear metal complexes and DACs needs to be further investigated. For homonuclear bimetal complexes, single-crystal X-ray diffraction, electrospray ionization mass spectrometry (ESI-MS), and liquid chromatography–mass spectrometry (LC-MS) are good characterization techniques. These techniques not only provide precise solid structures of bimetal complexes but also reveal their existence in solution, which is essential for checking the stability of the metal complexes during the catalytic process. However, for heteronuclear bimetal complexes, it is difficult to differentiate metal ions with similar ion radii by single-crystal X-ray diffraction analysis; thus, the precise determination of these complexes should combine with the results of other characteristic techniques such as X-ray photoelectron spectroscopy, elemental analysis, and so on, which can provide useful information to support the crystal structure obtained from X-ray diffraction. Actually, the most challenging is the structural determination of DACs synthesized by the pyrolysis method, which mainly relies on HAADF-STEM and X-ray absorption spectroscopy (XAS). However, neither of these techniques can provide direct evidence for the existence of dual-metal active sites. In HAADF-STEM imaging, the projection of dual-atom pairs is random, making it extremely difficult to accurately distinguish dual-atom pairs and single atoms on the supports. In some cases, scattering clusters or nanoparticles may be overlooked, which usually misleads the analysis of XAS data. Moreover, the structural information obtained from HAADF-STEM is the local environment in DACs. In this case, the analyzed structure–activity relationships may be inaccurate or even false. To accurately reveal the catalytic pathways and reaction mechanism, it is essential to develop advanced in situ characterization techniques, such as in situ scanning transmission electron microscopy (STEM), in situ XAS, and in situ Fourier transform infrared and Raman spectroscopies, which can provide valuable information on the reaction intermediates and give solid evidence for mechanism studies.

Third, the applications explored for DACs are limited. Most current researches of DACs focus on the activation and conversion of common small molecules such as CO₂, N₂, O₂, H₂O, etc., where DMSC between two metal sites can be generated and exploited for activity enhancement. Based on the reported catalytic mechanism of DACs for CO₂ reduction, the two metal sites usually play different roles in boosting the catalytic reactions, either with direct synergistic catalysis or indirect synergistic catalysis. In comparison to SACs, DACs also show superiority in producing C₂₊ products during CO₂ reduction. The formation of C₂₊ products usually consists of the formation of *CO/*CHO intermediates and C–C coupling between *CO/*CHO intermediates. DACs with two sufficiently close catalytic sites benefit the C–C coupling between two *CO or *CHO intermediates to generate C₂₊

products. In addition, DACs with well-defined structures can also let us understand how the C–C coupling occurs between *CO/*CHO intermediates. However, so far we still do not know how short of a distance between two catalytic sites will trigger the C–C coupling reaction. Besides the activation and conversion of the small molecules mentioned above, the close distance between two metal sites also enables them to catalyze some reactions by a cascade mode, especially for heteronuclear bimetal catalysts where two different metal sites can act with different catalytic functions. Therefore, more renewable energy-driven organic synthesis reactions that can generate high-value-added products by DACs are expected. This will be a new direction for the application of DACs.

In all, despite that several significant points of DACs should be addressed, as a type of emerging catalyst with more advantages over SACs, DACs will demonstrate more extensive applications in the future. We believe DACs will become the new research hotspot following SACs.

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Notes

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