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Confinement of Cu(I) single-atom site with asymmetric coordination modulation in defective metal-organic frameworks for photocatalysis

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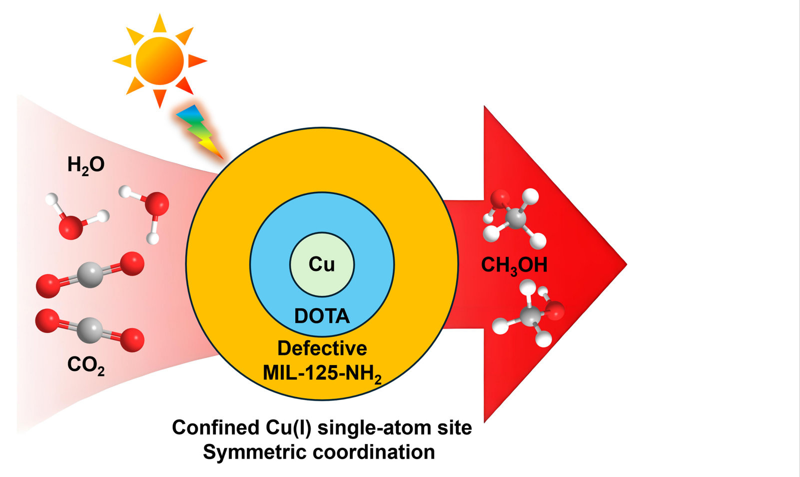

Photocatalytic CO_2 reduction is a sustainable strategy that converts solar energy into chemical energy, addressing both global warming and the fossil fuel crisis[1-3]. However, the dissociation energy of the C=O bond in the CO_2 molecule is as high as 805 kJ·mol^{-1}[4], making CO_2 highly stable and difficult to activate. In recent years, Metal-organic frameworks (MOFs) have attracted significant research interest in photocatalytic CO_2 reduction due to their highly adjustable structures and versatile compositional characteristics. MOFs can not only efficiently capture CO_2[5] but also optimize their band structures and facilitate the separation of photogenerated charge carriers through strategies such as linker engineering[6], metal node engineering[7], and defect engineering[8]. Compared with traditional inorganic semiconductors, MOFs offer unique advantages in photocatalytic CO_2 reduction[9,10]. Currently, the main product of photocatalytic CO_2 reduction with MOF systems is mostly CO[11] or CH_4[12]. Limited research focuses on the CH_3OH product[13], and the yield and selectivity still need to be improved. Moreover, the use of sacrificial agents and the

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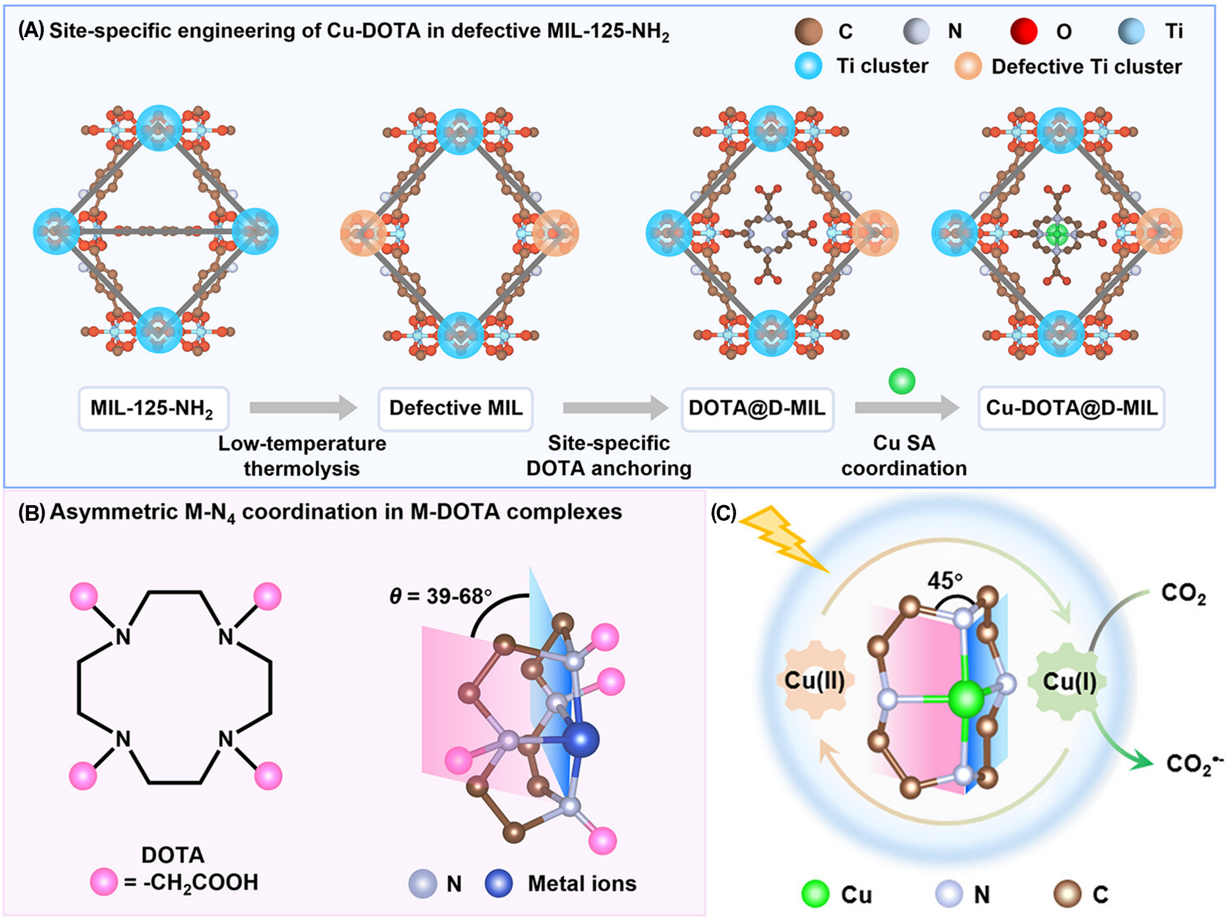

Figure 1. (A) Site-selective anchoring of Cu-DOTA within D-MIL; (B) Asymmetric M-N$_4$ coordination in the complex; (C) Electron transfer pathway in CO$_2$. This figure is adapted with permission from Ref.[15]. Copyright 2026 American Chemical Society. DOTA: N-heteromacrocyclic ligand tetraxetan; D-MIL: defective MIL-125-NH$_2$; SA: single-atom.

lack of rigorous validation raise concerns about the true source of CH_3OH product[14].

Recently, Dr. Yuanyuan Zhao, Prof. Guangshan Zhu, Prof. Hongzhu Xing, and coworkers reported a site-specific asymmetric coordination engineering strategy to construct a high-performance defective MIL-125-NH$_2$ (D-MIL) photocatalyst with Cu single-atom (SA) sites for highly selective CO_2 reduction to CH_3OH[15]. First, the researchers prepared D-MIL with unsaturated Ti-oxo clusters via low-temperature pyrolysis. Then, the flexible N-heteromacrocyclic ligand tetraxetan (DOTA) was anchored at the defective sites to repair the missing-linker defects. Finally, Cu(II) ions were chelated with DOTA to form the target catalyst Cu-DOTA@D-MIL [Figure 1A]. X-ray absorption fine structure (XAFS) analysis and density functional theory (DFT) simulations confirm that Cu SA is coordinated with four N atoms of DOTA to form an asymmetric Cu-N$_4$ configuration with a dihedral angle of 45° [Figure 1B], which effectively suppresses the aggregation of Cu species and stabilizes the active sites.

Notably, the ultrahigh formation constant of Cu-DOTA ($\log \beta_{Cu} = 22.3$) endows the catalyst with excellent structural stability. The D-MIL support not only provides suitable anchoring sites for the DOTA but also maintains the original crystallinity and disk-like morphology. Meanwhile, the incorporation of Cu-DOTA alters the conduction band position of the catalyst, making it closer to the reduction potential of CO_2-to-CH_3OH (-0.38 V *vs.* NHE) and more favorable for the conversion. *In situ* electron paramagnetic resonance results under light irradiation, along with cyclic voltammetry measurements, indicate that the

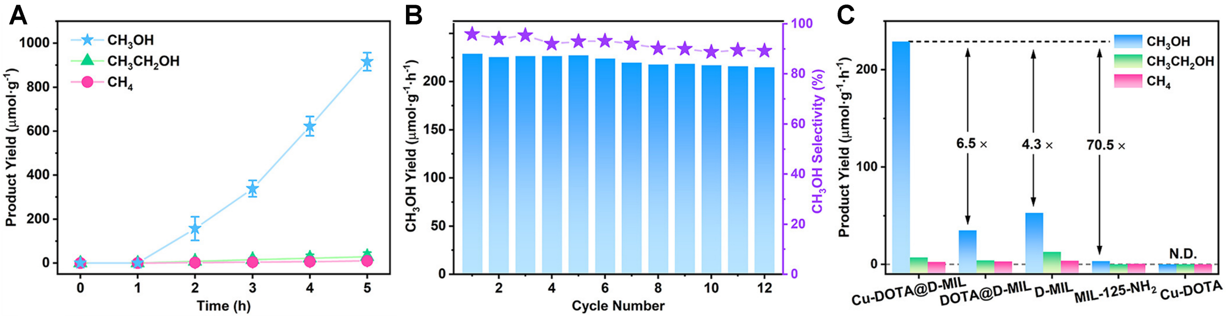

Figure 2. (A) Product yields of CH_3OH, CH_3CH_2OH, and CH_4 over Cu-DOTA@D-MIL during the photocatalytic CO_2 reduction process; (B) Stability cycling tests over Cu-DOTA@D-MIL; (C) Product yields over Cu-DOTA@D-MIL, DOTA@D-MIL, D-MIL, MIL-125-NH_2, and Cu-DOTA. This figure is adapted with permission from Ref.[15]. Copyright 2026 American Chemical Society. DOTA: N-heteromacrocyclic ligand tetraxetan; D-MIL: defective MIL-125-NH_2.

catalyst follows a cascade electron transfer pathway. The photogenerated electrons reduce Cu(II) to stable Cu(I) active sites, which further mediate fast electron transfer to activate CO_2 and are themselves oxidized back to Cu(II). The asymmetric Cu-N_4 coordination microenvironment sustains the Cu(I)/Cu(II) redox cycle and avoids over-reduction to Cu(0), providing a steady electron supply for selective CO_2 conversion [Figure 1C].

Under visible-light irradiation without any sacrificial agent, Cu-DOTA@D-MIL exhibits excellent photocatalytic CO_2 reduction performance, achieving a CH_3OH yield of 229.0 $\mu mol \cdot g^{-1} \cdot h^{-1}$ with a selectivity of up to 95.9% [Figure 2A]. Control experiments confirm the photocatalytic property of the conversion and the indispensability of CO_2. Isotopic labeling experiments with $^{13}CO_2$ further verify that the produced CH_3OH is exclusively derived from CO_2. The catalyst also shows excellent stability, maintaining about 93.8% of its initial CH_3OH yield after 12 consecutive cyclic runs [Figure 2B]. Powder X-ray diffraction, transmission electron microscopy, X-ray photoelectron spectroscopy, and XAFS characterizations prove the robustness of Cu-DOTA@D-MIL. The Cu-DOTA complex alone shows no catalytic activity, while the combination of these components significantly boosts the CH_3OH production rate, which is 70.5 times higher than that of pristine MIL-125-NH_2 [Figure 2C][15].

Mechanistic investigations reveal that the superior catalytic results should be attributed to the asymmetric Cu-N_4 coordination microenvironment, which modulates the electronic structure of Cu SA and facilitates the formation and stabilization of Cu(I) active sites. As a result, the Gibbs free energies to yield key reaction intermediates such as *CO and *CHO are significantly reduced by 0.07 and 0.50 eV, respectively, while the formation of byproducts including HCOOH and CO is suppressed [Figure 3]. In contrast, the Cu(II) site proceeds via a thermodynamically unfavorable pathway, as evidenced by the highly endothermic $^*OCH_2$-to-$^*CH_2OH$ rate-determining step ($\Delta G = +1.53$ eV) and the transition from Cu-O to Cu-C adsorption state.

In summary, MOF defect engineering and site-specific macrocyclic ligand functionalization are innovatively integrated to design a novel photocatalyst with an asymmetric coordination environment. The emerging and rare research strategy is deployed in photocatalytic CO_2 to CH_3OH reduction without a sacrificial agent. The high yield and selectivity of CH_3OH highlight the importance of precise integration of each functional module in the catalyst design. This work not only addresses the critical issues of metal aggregation and active site oxidation in SA catalysts but also provides a new approach to regulate the catalytic reaction pathway by engineering the local coordination field of atomic sites. The asymmetric coordination engineering offers a new perspective on the development of high-selectivity, high-stability photocatalysts for CO_2 conversion, and deepens the mechanistic understanding of solar-driven CO_2 reduction catalysis.

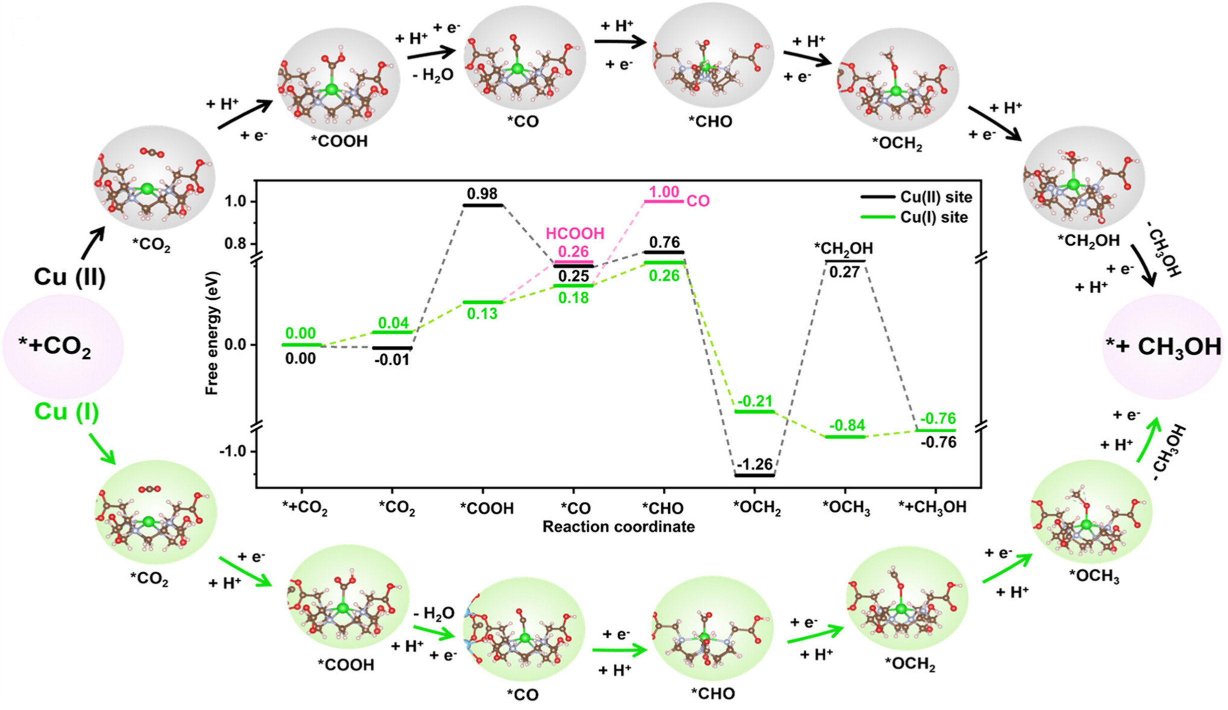

Figure 3. Proposed reaction routes and intermediate structures for CO_2-to-CH_3OH reduction over Cu(II) and Cu(I) active sites. This figure is adapted with permission from Ref.[15]. Copyright 2026 American Chemical Society.

DECLARATIONS

Authors' contributions

Drafted the manuscript: Wang, L.
Revised and rewrote sections of the manuscript: Zhang, C.; Zhang, J.

Availability of data and materials

Not applicable.

AI and AI-assisted tools statement

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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