

Cite this: *Chem. Sci.*, 2024, 15, 14081

Recent advances of metal active sites in photocatalytic CO₂ reduction

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Photocatalytic CO₂ reduction captures solar energy to convert CO₂ into hydrocarbon fuels, thus shifting the dependence on rapidly depleting fossil fuels. Among the various proposed photocatalysts, systems containing metal active sites (MASs) possess obvious advantages, such as effective photogenerated carrier separation, suitable adsorption and activation of intermediates, and achievable C–C coupling to generate multi-carbon (C₂₊) products. The present review aims to summarize the typical photocatalytic materials with MAS, highlighting the critical role of different formulations of MAS in CO₂ photoreduction, especially for C₂₊ product generation. State-of-the-art progress in the characterization and theoretical calculations for MAS-containing photocatalysts is also emphasized. Finally, the challenges and prospects of catalytic systems involving MAS for solar-driven CO₂ conversion are outlined, providing inspiration for the future design of materials for efficient photocatalytic energy conversion.

Received 25th March 2024
Accepted 22nd July 2024

DOI: 10.1039/d4sc01978d

rsc.li/chemical-science

1 Introduction

Over-reliance on fossil fuels as energy carriers leads to excessive CO₂ emissions from combustion, which in turn causes climate change, environmental damage and energy crisis.^{1–3} Shifting from fossil fuels to renewable energy sources to achieve carbon neutrality is an important step towards sustainable development. Therefore, there is an urgent need to find a suitable, effective, and green strategy to facilitate the conversion of CO₂ and access renewable energy through sustained technological innovation.

CO₂ capture and conversion by artificial photosynthesis can simultaneously address the rising global CO₂ emissions and produce hydrocarbon fuels to accomplish carbon neutrality.^{4–6}

It is proving to be an elegant and promising solution, attracting the interest of scientists and making great strides in the efficiency of CO₂ conversion.^{7–11} Specifically, the photocatalytic reduction of CO₂ achieves a sustainable alternative to conventional fossil fuels, which is carried out in relatively mild conditions-room temperature and pressure, driving the conversion of CO₂ to hydrocarbons directly without additional energy supply or harmful substance release. Photocatalytic CO₂ reduction consists of three main processes:¹² the catalyst generates electron–hole pairs under sunlight;^{13–15} carriers separate and migrate to the surface;¹⁶ CO₂ is activated and converted at the surface active sites, involving C–O bond breaking, C–H bond formation, and C–C coupling.^{17,18} In fact, the CO₂ molecule possesses a rather stable structure with high dissociation energy to cleave the C=O bond (750 kJ mol^{−1}), which poses a challenge for the activation and conversion of CO₂.¹⁹ In addition, solar-driven CO₂ reduction involves complex multi-step conversions that, depending on the number of electrons and protons transferred, produces CO,^{20–22} CH₃OH,^{23–25} CH₄,^{26,27} C₂H₄,^{28–30} C₂H₆,^{31,32} C₂H₅OH,³³ etc. Due to the diversity of products of CO₂ photoreduction, achieving highly selective CO₂ conversion to generate specific target products is extremely challenging.

Various strategies have been employed to improve the efficiency and selectivity of CO₂ photoreduction, including enhancing light absorption,^{34,35} promoting carrier separation,³⁶ constructing active sites,³⁷ and promoting C–C coupling.³⁸ According to the current findings, MAS possesses significant advantages in improving the performance of photocatalytic reduction of CO₂ and promoting C–C coupling to obtain C₂₊ products.^{39–41} This review mainly introduces the research

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progress of MAS in driving photocatalytic CO₂ conversion (Fig. 1). Photocatalytic systems containing MAS including metal oxides, metal sulfides, layered double hydroxides (LDHs), metal organic framework (MOF), covalent organic frameworks (COF), single atom catalysts, and metal complexes are summarized. The achievement of MAS with different formulations in photocatalytic CO₂ conversion is systemically explored while mechanisms that drive performance improvement are discussed in detail. The development of characterization techniques and theoretical calculation to determine the structure and function of MAS in CO₂ photoreduction is also highlighted. Finally, the difficulties, challenges, and novel viewpoints of feasible solutions are addressed regarding the design of advanced photocatalysts containing MAS for efficient solar energy conversion.

2 Photocatalytic systems with MAS

Micro-nanostructures containing MAS, including metal oxides, metal sulfides, LDHs, MOF, COF, single atom catalysts, and metal complexes are widely used in photocatalytic CO₂ reduction. According to the process and mechanism of CO₂ photoreduction, the catalytic systems with high light absorption capacity, sufficient carrier separation, and abundant active sites show obvious advantages in the yield and selectivity of CO₂ conversion.

2.1 Metal oxides

In the complex and diverse photocatalytic systems, metal oxides have become the most representative and well-established photocatalysts. A large number of strategies aimed at modulating the band gap, facilitating carrier separation, and establishing active sites have been proposed and intensively investigated in metal oxides.^{42–44} TiO₂, as a representative metal oxide, has become a photocatalyst of wide interest due to its low toxicity, high stability and economic advantages. Defect engineering, heterostructure construction, heteroatom doping, and surface modulation have been proposed to regulate the carrier

migration, CO₂ adsorption and activation of TiO₂-based catalysts. The synergistic effect of Ru and oxygen vacancies (Vo) on the photocatalytic performance of TiO₂ (Ru-TiO_{2-x}) was systematically investigated.⁴⁵ It was found that Ru-TiO_{2-x} exhibited high activity for the photoreduction of CO₂ to CH₄. The introduced Vo in Ru-TiO_{2-x} provided important contributions to promote photogenerated carrier separation and facilitate CO₂ conversion. The Ru species effectively captured photogenerated electrons, which inhibited further photogenerated carrier recombination.

Photocatalytic CO₂ reduction for the generation of C₂₊ products was achieved in metal-oxide systems. The vacancy-rich TiO₂ with Cu single atoms loading produced C₃H₈, which involved an overall 20 e⁻ reduction and two sequential C-C coupling processes.⁴⁶ The Cu-Ti-V_O unit in the Ti_{0.91}O₂ matrix was formed through the modulation of the electronic coupling interaction between the Cu atoms and adjacent Ti atoms by Vo. This unique unit lowered the energy levels of the key *CHOCO and *CH₂OCOCO intermediates, thereby tuning the C₁-C₁ and C₁-C₂ couplings to thermodynamically favourable exothermic processes (Fig. 2a). Moreover, the metastable hexagonal WO₃ (h-WO₃), offering a suitable bandgap, exhibited efficient photoreduction of CO₂ to C₂H₄.⁴⁷ The blue color of the metastable state of WO₃ was attributed to the reduction of W⁶⁺ to W⁵⁺ or W⁴⁺ with the increase of the reduced state, which indicated the existence of Vo. The surface Vo enhanced the light absorption capability and promoted the photogenerated carrier separation. More importantly, the W-S-W sites formed by the S atom,

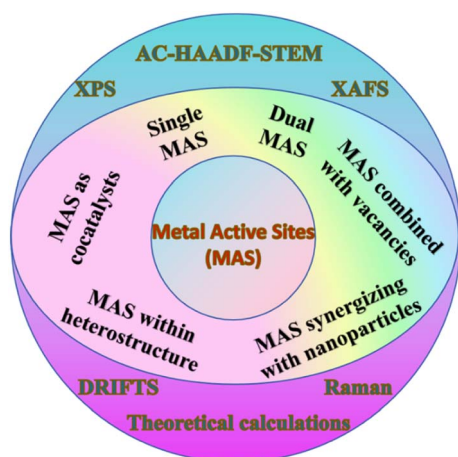


Fig. 1 Overview of the metal active sites in photocatalytic CO₂ reductions.

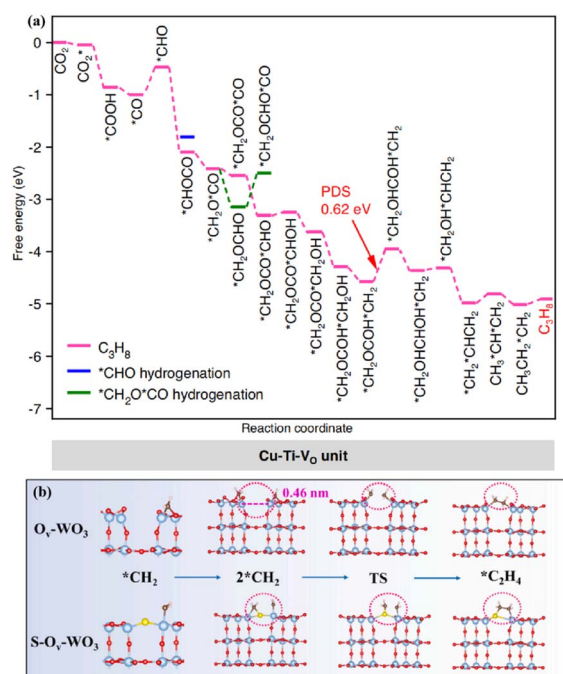


Fig. 2 (a) Gibbs free energy diagrams of CO₂ reduction on the Cu-Ti-V_O unit. This figure has been reproduced from ref. 46 with permission from Springer Nature, copyright 2023. (b) The C-C coupling process of Ov-WO₃ and S-Ov-WO₃. This figure has been reproduced from ref. 47 with permission from Elsevier, copyright 2023.



which replaced oxygen atoms and bridged the adjacent W atoms, benefited the adsorption of $^*\text{CH}_2$ intermediates and promoted the C–C coupling to generate C_2H_4 (Fig. 2b).

Based on the above analysis, the MAS constructed in the metal oxide system is structurally stable, successfully achieving efficient photocatalytic CO_2 conversion with C_{2+} generation. In fact, MAS in metal oxides often synergizes with defect and doping atoms to achieve performance enhancement. Therefore, MAS introduced in metal oxides usually needs multi-step experimental treatment processes.

2.2 Transition metal sulfides/phosphorus sulfides

Various metal chalcogenides, such as ZnS, CdS, MnS, CdSe, ZnIn_2S_4 (ZIS), and CuIn_5S_8 , have exhibited progressive photocatalytic performances. Their excellent properties, including their low cost, wide range of light absorption, and high carrier mobility, have made them one of the most promising materials for CO_2 conversion.

The reduction potential of ZnS is -1.04 V vs. NHE, which is relatively negative and particularly suitable for the photocatalytic reduction reaction.⁴⁸ However, the wide band gap (3.6–3.8 eV), fast recombination of the charge carriers, and low selectivity toward CO_2 reduction competing with the hydrogen evolution reaction (HER) limit the efficiency of ZnS. Cu-doped ZnS, containing abundant sphalerite and wurtzite phase (S–W) junctions, enhanced the photocatalytic activity with high CO selectivity.⁴⁹ The S–W phase junction containing abundant sulfur vacancies (V_S) effectively facilitated the separation of charge carriers and the localization of photoelectrons for surface catalysis. The addition of Cu increased the electron density at the Fermi energy level, promoted the reactivity of the Cu sites, and enhanced the bonding of the catalyst surface to the $^*\text{CO}$ intermediate, thereby improving the CO selectivity. Furthermore, the dual functional ZnS coupled with $g\text{-C}_3\text{N}_4$ simultaneously enhanced the surface and bulk carrier separation of $g\text{-C}_3\text{N}_4$ for the highly selective reduction of CO_2 to CH_4 .⁵⁰ ZnS acted as a cocatalyst to capture the photogenerated electrons of $g\text{-C}_3\text{N}_4$. It contributed a polarization electric field, which was created inside the ZnS nanoparticle along the direction of spontaneous polarization, to prompt the migration and separation of photogenerated charges from bulk to surface.

ZIS, belonging to the AB_2X_4 group of ternary compounds, has been used in photocatalysis with visible light absorption.⁵³ The metallic ZnIn_2S_4 , which is rich in indium vacancies (V_In), exhibited full-spectrum responsiveness for high CO_2 photoreduction efficiency.⁵¹ The V_In defect state captured the excited hole (h^+) and increased the minority carrier diffusion length, resulting in a large number of carriers moving to the surface and participating in the conversion of CO_2 . Theoretical calculations revealed that V_In lowered the energy barrier of the rate-limiting step (the formation of COOH^* , Fig. 3a and b), leading to the high rate of CO evolution. In addition, anchoring single Au atoms to ultrathin ZIS (Au_1/ZIS) nanosheets with V_S resulted in the $\text{Au}_1\text{-S}_2$ low coordination structure, which enabled exceptional photocatalytic CO_2 -to- CH_4 conversion.⁵² The introduction of Au single atoms enhanced the efficiency of carrier

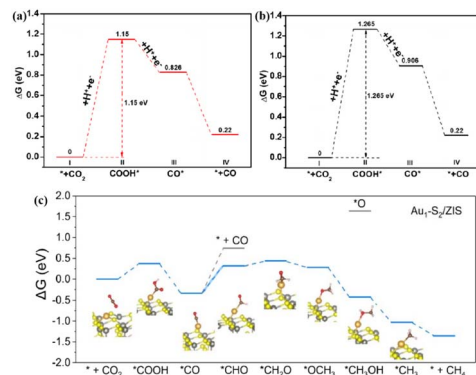


Fig. 3 Free energy diagrams for the reduction of CO_2 to CO over the (001) facets of V_In -rich-ZIS (a) and V_In -poor-ZIS (b). These figures have been reproduced from ref. 51 with permission from American Chemical Society, copyright 2022. Free energy diagrams of photocatalytic CO_2 to CH_4 for $\text{Au}_1\text{-S}_2/\text{ZIS}$ (c). This figure has been reproduced from ref. 52 with permission from Wiley-VCH, copyright 2022.

separation and transfer. Moreover, the low-coordinated single Au atom significantly enhanced CO_2 activation, lowered the energy barrier for $^*\text{CO}$ protonation, and stabilized the $^*\text{CH}_3$ intermediate, leading to the selective generation of CH_4 by CO_2 photoreduction.

Transition metal phosphorous trichalcogenides have been well-explored in the photoreduction of CO_2 to valuable fuels. The introduction of V_S in AgInP_2S_6 regulated the CO_2 photoreduction reaction pathway to steer the dominant generation of C_2H_4 .⁵⁴ The V_S led the charge accumulation on the Ag atoms near V_S , which effectively captured the forming $^*\text{CO}$. This phenomenon enriched the catalyst surface with key reaction intermediates and promoted C–C coupling to generate C_2 species with low binding energy barriers. In addition, the tandem synergistic effect of the charge-enriched Cu–In dual site, which was confined on the lateral edge of the CuInP_2S_6 monolayer, became the main reason for the efficient conversion and high selectivity of C_2H_4 .⁵⁵ In the presence of light, the limbic In site of the CuInP_2S_6 monolayer converted CO_2 mainly to $^*\text{CO}$, which was transferred to the neighbouring Cu site for the subsequent C–C coupling reaction to C_2H_4 .

By reason of the foregoing, MAS in metal chalcogenides shows unique advantages in the generation of C_{2+} products. However, due to the limitation of the stability of the metal sulfide, the stability of MAS in them may be lacking. Therefore, in photocatalytic applications, attention should be paid to improving the stability of MAS in metal sulfides.

2.3 LDHs

LDHs are typically layered materials consisting of laminates and interlaminar anions with a high degree of flexible tunability in terms of morphology and ionic composition.⁵⁷ The adjustment of the metal cation or anion in LDH can easily regulate the electronic structure and influence the CO_2 conversion process. For example, the selectivity of the photocatalytic reaction could be precisely tuned by the composition of metal cations in the ZnM-LDH photocatalysts ($\text{M} = \text{Ti}^{4+}, \text{Fe}^{3+}, \text{Co}^{3+}, \text{Ga}^{3+}, \text{Al}^{3+}$).⁵⁶



Specifically, the main reduction product of ZnTi-LDH was CH₄. ZnFe-LDH and ZnCo-LDH generated H₂ by water splitting, and ZnGa-LDH and ZnAl-LDH produced CO (Fig. 4a and b). Experimental characterization and theoretical calculations revealed that the d-band center of the M³⁺ or M⁴⁺ cations affected the adsorption strength of CO₂: cations with the d-band centers close to the Fermi level adsorbed CO₂ strongly, benefiting CH₄ or CO formation. Conversely, the deviation of the d-band centre from the Fermi level led to poor CO₂ adsorption and hence H₂ production. In addition, the strategies involving morphology modulation, heterostructure construction, doping, and defect introduction have a crucial effect on the CO₂ conversion process of LDH. The S-scheme heterojunction of g-C₃N₄/CoCo-LDH preserved the water oxidation ability of CoCo-LDH and redox ability of g-C₃N₄.⁵⁸ The atomic-level interface chemical bond (Co–N₂ bond) of g-C₃N₄/CoCo-LDH realized the high-speed transfer of electrons. The addition of CoCo-LDH benefited the CO₂ adsorption, reduced the energy barrier of the key intermediate *COOH, and promoted water decomposition.

Obviously, MAS can take advantage of the two-dimensional (2D) structure, as well as the highly flexible adjustability in the morphology and ionic composition of LDH. However, the synergies of different metals and their roles in C₂₊ generation remain to be explored.

2.4 MOF

One of the crystalline porous materials, MOF, which possesses diversified metal ions/clusters and organic linkers, as well as atomically precise and tailorable structures, provides the natural MAS for catalysis.⁶⁰ Zirconium-based MOF (PCN-222) hybridized with cellulose acetate (CA@PCN-222) increased the activity of CO₂ photoreduction to formate compared with pristine PCN-222 by regulating the atomic interface structure of the MAS (Fig. 5a).⁵⁹ The valence band (VB) across the Fermi energy levels resulted in higher charge-transfer kinetics of CA@PCN-222 relative to PCN-222. The interfacial electron transfer from

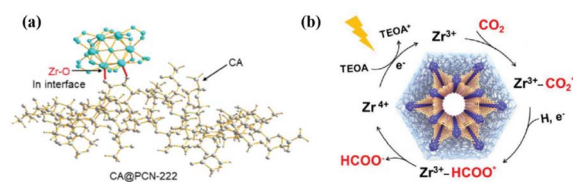


Fig. 5 (a) Schematic atomic interface model of CA@PCN-222. (b) Proposed mechanism for the CO₂ photoreduction reaction over CA@PCN-222. These figures have been reproduced from ref. 59 with permission from Wiley-VCH, copyright 2023.

CA to PCN-222 led to the redistribution of the Zr d-orbital electrons. Moreover, the Zr^{IV}-cluster unit in CA@PCN-222 was turned into a Zr^{III}-cluster active site after accepting two electrons from two adjacent tetrakis(4-carboxyphenyl)-porphyrin ligands under visible-light irradiation, which selectively reduced CO₂ to HCOO[−] in a two-electron process (Fig. 5b).

The modulation of the coordination environment around the MAS in MOFs helps to reveal the relationship between structure and activity during CO₂ photoreduction. In UiO-type MOFs bearing bipyridine linkers, the number of coordinated N atoms around a single Co site was tuned to provide UiO-Co-N_x (x = 2, 3 and 4) for photocatalytic CO₂ reduction.⁶¹ UiO-Co-N₃ exhibited superior activity to the other counterparts, which was mainly attributable to the difference in the number of coordinating N atoms around the Co site. Particularly, UiO-Co-N₃ endowed the lowest energy barriers of the rate-determining step (CO₂ → COOH*) and the desorption of CO* among all UiO-Co-N_x samples, accounting for the optimized CO₂ photoreduction activity.

The MAS in MOF enables liquid C₂₊ generation. The specific NH₂–Cu–NH₂ triple atom site was constructed by incorporating Cu sites into the connected nodes of defective UiO-66-NH₂, realizing photocatalytic CO₂-to-acetone conversion.⁶² Specifically, one of the N active sites on the NH₂–Cu–NH₂ adsorbed CO₂ and converted CO₂ to form *CH₃ (CO₂ → COOH* → CO* → *CH₃). Meanwhile, the Cu site activated its adsorbed CO₂ to CO*. *CH₃ and *CO underwent the first C–C coupling on CuN₂O₂ to generate *CO–*CH₃. At the same time, another N site on the CuN₂O₂ fragment activated the adsorbed CO₂ into CO*, which underwent a second C–C coupling process with the *COCH₃ intermediate to generate the crucial *COCOCH₃. Due to the synergistic interaction between the Cu site and the N site, the C₂ intermediate on the CuN₂O₂ ultimately generated C₃.

In summary, the MAS in MOF connected with organic ligands exhibits good dispersion and high utilization, which can make full use of the porous property of MOF to optimize the photocatalytic CO₂ reduction performance. However, its synthesis process involves complex chemical reactions and utilizes expensive organic ligands, making practical production applications difficult.

2.5 COF

COF is a class of organic polymers linked by reversible covalent bonds, which possesses periodical structures, well-defined porosity, an extended π-conjugated framework, and pore

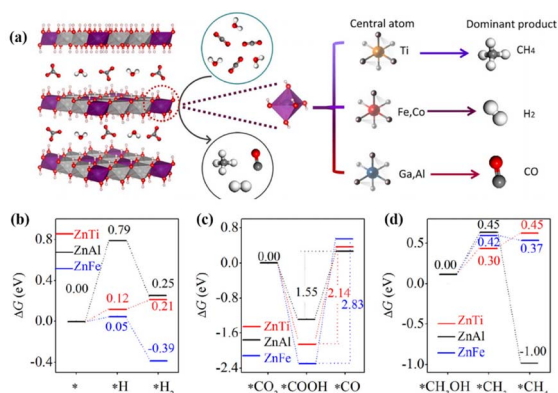


Fig. 4 (a) Scheme showing CO₂ and H₂O photoreduction on the different ZnM-LDH photocatalyst (carbon: dark gray; oxygen: red; hydrogen: white). DFT calculations of the elementary steps of (b) H₂ evolution, (c) CO₂ reduction to CO, and (d) CO₂ reduction to CH₄ involving a methanol intermediate over ZnTi-LDH, ZnAl-LDH, and ZnFe-LDH. These figures have been reproduced from ref. 56 with permission from Elsevier, copyright 2020.



structures for mass transfer. An adequate MAS of COF could be constructed by incorporating metal atoms into the skeletons or pore channels by coordination interaction.⁶³ 2D COF ultrathin nanobelts coordinated with single Cu–O/N sites (Cu²⁺ anchored by both O and N) exhibited high CO selectivity of 94% under visible-light-driven CO₂ reduction.⁶⁴ Crucially, the Cu–O/N sites benefited the electron transfer from COF upon light irradiation, and served as the active sites for the highly selective reduction of CO₂ to CO. Two types of cobalt Schiff base COF composites, Co-2,3-DHTA-COF with Co–O₄ sites and Co-TP-COF with Co–O₃N sites, realized the CO₂ photoreduction into CO (Fig. 6).⁶⁵ The supereminent photocatalytic performance of Co-COF with Co–O₄ sites was mainly attributed to the high CO₂ adsorption capacity, low charge-transfer resistance, strong separation of electrons and holes, and the lower energy barrier in the ligand exchange process between Co-2,3-DHTA-COF and CO₂. For hydrocarbon product generation, single-atom MoN₂ sites were introduced into COF (Mo-COF) to realize the photoreduction of CO₂ to CH₄ and C₂H₄ under visible light.⁶⁶ The MoN₂ sites contributed to the efficient separation efficiency of photo-generated electrons and holes, enhanced the adsorption and activation of CO₂ and CO, and reduced the energy barriers for the formation of hydrocarbon intermediates, thus leading to the production of high value-added hydrocarbons over Mo-COF.

Particularly, MAS can utilize the π -conjugated framework in COF to promote the photogenerated carrier separation and enhance the photocatalytic CO₂ reduction. However, MAS needs to be grafted onto the COF structure with fine regulation. In addition, the construction of multiple MAS in COF and the study of their catalytic mechanism still need to be continuously explored.

2.6 Single-atom catalysts

Single-atom catalysis with MAS uniformly and individually loaded on a supporting material provides a research platform for structure–performance correlation at the atomic level. Atomically dispersed MAS improves the atomic utilization, modulates the charge distribution of the catalyst, and affects the adsorption and conversion of reactants and intermediates, ultimately influencing the product efficiency and selectivity of the photocatalytic CO₂ reduction.

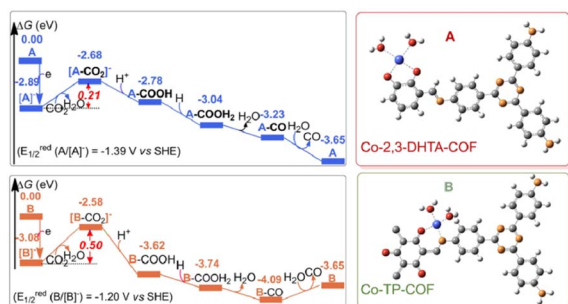


Fig. 6 Gibbs energy profiles of the CO₂RR-to-CO reaction over Co-2,3-DHTA-COF (A, blue line) and Co-TP-COF (B, orange line). This figure has been reproduced from ref. 65 with permission from American Chemical Society, copyright 2023.

Loading rare-earth La single atoms on carbon nitride (O/La–CN) constructed the active centers of La–N charge-transfer bridges for photocatalytic CO₂ reduction.⁶⁷ Electronic state changes induced by the hybridization of the 4f and 5d orbitals of La single atoms and the p–d orbitals of La–N atoms established charge-transfer channels for La–N bridges to promote carrier separation. Bader charge and differential charge distributions suggested that electrons were transferred through La atoms into connected N atoms, and eventually through C atoms to O atoms. The O/La–CN strengthened CO₂ adsorption, endowed the high capacity for CO₂ uptake, and reduced the activation energy barrier for COOH* formation. Moreover, the desorption of CO from the surface of O/La–CN required the lowest energy (0.2 eV) compared with the dissociation reaction (COH*, 2.96 eV and C* + H₂O, 4.59 eV) or hydrogenation (HCO*, 1.53 eV), contributing CO formation with high selectivity (Fig. 7a). Cu loading on BiOBr nanosheets (Cu₁@BiOBr) established a strong built-in electric field with isolated Cu sites that acted as electron traps to promote charge transfer and stabilize charge carriers.⁶⁸ The high selectivity of methanol within this photocatalytic system could be ascribed to the energy-favorable hydrogenation of the *CO intermediate into *CHO (Fig. 7b). Furthermore, the unfavorable adsorption of CH₃OH on Cu₁@BiOBr relative to H₂O prevented methanol from being oxidized by photogenerated holes.

In addition to single MAS loading, dual MAS incorporation has been explored to drive CO₂ photoreduction with diverse functions. The dual MAS of cobalt (Co) and ruthenium (Ru) supported on a conjugated porous carbon nitride polymer exhibited efficient photocatalytic CO₂ reduction.⁶⁹ *In situ* characterizations and theoretical calculations revealed that the active Co sites facilitated dynamic charge transfer, along with Ru working as adsorption sites for CO₂ photoactivation. In detail, the atomic Co facilitated dynamic electron transfer from

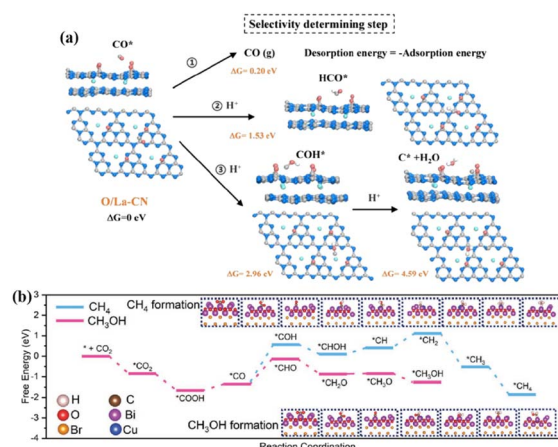


Fig. 7 (a) Calculated free energy for the photocatalytic CO₂ reduction reaction of the selectivity-determining step. This figure has been reproduced from ref. 67 with permission from American Chemical Society, copyright 2020. (b) The DFT-calculated free energy diagram for the hydrogenation of CO₂ to CH₃OH and CH₄ over Cu₁@BiOBr. This figure has been reproduced from ref. 68 with permission from Wiley-VCH, copyright 2023.

the carbon nitride polymer to the atomic Ru site, resulting in the COOH* intermediate being effectively stabilized by the charged-rich Ru site. Moreover, the smaller Gibbs free energy of CO formation than that of the protonation of CO* to CHO* resulted in high CO selectivity. Similarly, Ru and Cu single atoms simultaneously incorporated into polymeric carbon nitride (poly-CN) exhibited higher selectivity (95%) for CH₄ production than that decorated with Ru or Cu individually.⁷⁰ The atomically dispersed Ru-N₄ and Cu-N₃ sites tuned the electronic structure of poly-CN, and were identified as active centers. During CO₂ photoreduction, the Ru single atom was essential for proton production, while the Cu single atom played a dominant role in the reduction process. Due to the thermodynamically more favorable conversion of *CO to *CHO, the coexistence of the Ru and Cu single atoms resulted in the efficient conversion of CO₂ to CH₄.

Remarkably, the MAS in single-atom catalysts exhibits high metal atom utilization and achieves synergistic effects of multiple MASs. However, the metal is easily aggregated to form particles during the construction process. Thus, a delicate experimental design is required to successfully construct MAS in single-atom form.

2.7 Metal complexes

The realization of CO₂ photoreduction by transition metal complexes with tunable and definable chemical structures is accompanied by the activation and immobilisation of neutral CO₂ molecules at the metal centre.⁷¹ By installing a 2-phenol, 2-amino or 2-mercapto to a tripodal skeleton, the Co-based homogeneous catalysts (named [CoN₃O]ClO₄, [CoN₄]ClO₄ and [CoN₃S]ClO₄, respectively) possessed different coordination microenvironments for CO₂ reduction.⁷² The optimal [CoN₃O]ClO₄ photocatalyst had a maximum turnover number (TON) of 5652 in photocatalytic CO₂ reduction among [CoN₄]ClO₄ and [CoN₃S]ClO₄. The strong electronegativity of the oxygen atom in the ligand endowed the Co(II) catalytic center with a low reduction potential and more stable *COOH intermediate, thus substantially promoting the CO₂-to-CO conversion. The dinuclear heterometallic [CuNiL²] showed the highest CO₂-to-CO conversion relative to dinuclear homometallic [Ni₂L²(CH₃-OH)₂] and mononuclear [NiL¹(CH₃OH)].⁷³ A theoretical calculation revealed that the introduction of inactive Cu^{II} in CuNi-L² promoted the transportation of photo-generated electrons to the coupled active Ni^{II} site. This allowed Ni^{II} with an O₄ coordination environment in [CuNiL²] to express strong reducing ability, which significantly accelerated the photocatalytic CO₂-to-CO conversion.

Metal complexes could drive C-C coupling to generate C₂₊ products. The synergistic dual sites of rhenium(I) bipyridine fac-[ReI(bpy)(CO)₃Cl] (Re-bpy) and copper porphyrinic triazine framework [PTF(Cu)] working in tandem strategy achieved the photocatalytic conversion of CO₂ to C₂H₄ (Fig. 8).⁷⁴ The CO generated at the Re-bpy sites was adsorbed by the nearby Cu single sites in PTF(Cu), followed by a synergistic C-C coupling process to ultimately produce C₂H₄. Critically, Re-bpy-*CO could enter the porous PTF(Cu) and move to the nearby Cu-*CO,

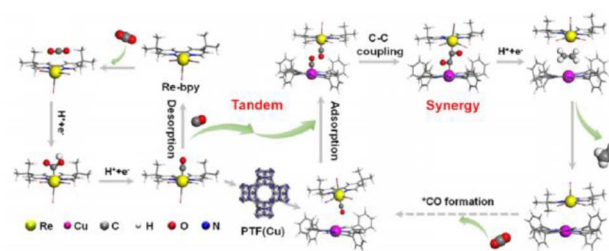


Fig. 8 Tandem catalysis mechanism of Re-bpy/PTF(Cu). This figure has been reproduced from ref. 74 with permission from American Chemical Society, copyright 2023.

leading to practicable free energy for the CO-CO coupling between Cu-*CO and Re-bpy-*CO (Re-bpy-*CO-*CO-PTF(Cu)). However, PTF(Cu) catalysts alone produced CO under similar conditions. This was caused by the large distance between the adjacent Cu centers in PTF(Cu) hindering C₂₊ formation *via* the coupling of Cu-*CO-*CO-Cu.

As mentioned above, the alteration of the MAS coordination environment can be achieved by modulating the skeleton in metal complexes, which in turn regulates the photocatalytic CO₂ reduction performance. It is conducive to revealing the in-depth reaction mechanism. However, the typical problems in photocatalysis, such as the high separation cost and low chemical stability, still limit their practical applications.⁷⁵

3 Different formulations of MAS in the photocatalytic CO₂ reduction

Incorporation of MAS can regulate the transport of photo-generated carriers, increase the local electron density of the adsorption sites, affect the adsorption strength of reactants and intermediates, and ultimately adjust the barrier and selectivity of the reaction. In this section, the role of different formulations of MAS in photocatalytic CO₂ reduction is described in detail (Table 1).

3.1 Single MAS

The incorporation of individual MAS into the catalyst backbone from an atomic level perspective maximizes atomic utilisation efficiency and optimizes the performance of photocatalytic CO₂ conversion. The bipyridine-based polyimide polymer (Bpy-PDI) anchoring single Ni site achieved diluted CO₂ photoreduction with high generation activity for CO₂-to-CO in 0.1 atm CO₂ pressure.⁷⁶ The obviously larger adsorption energy of CO₂ for the Ni site (1.44 eV) compared to that of Bpy-PDI (0.19 eV) indicated a much stronger adsorption affinity of the Ni site towards CO₂. Moreover, the free energy of COOH* generation (the rate-determining step) on the Ni sites (-0.07 eV) was obviously smaller than that of Bpy-PDI (1.69 eV), revealing the contribution of the dispersed Ni atom toward the energy barrier decline. Cu single atoms on the nitrogen-doped carbon anchored on TiO₂ with the anatase-rutile mixed phase exhibited 100% CO selectivity in the photocatalytic CO₂ reduction.⁷⁷ Cu single atoms became the adsorption and activation sites for



Table 1 Different formulations of MAS in photocatalytic CO₂ reduction

| Single MAS | Catalyst | Reactive sites | Light source | Reaction condition | Performance ($\mu\text{mol g}^{-1} \text{h}^{-1}$) | Ref. |
|---|--|--|---|--|--|----------|
| Cu-doped ZnS containing abundant S-W junctions | Cu | Cu | 300 W Xe lamp | 18 mL solution containing chloroform + 2 mL 2-propanol + CO ₂ | CO: 68.9 (99.9%) | 49 |
| V _{In} -rich-ZIS | V _{In} | V _{In} | 300 W Xe lamp AM 1.5 cut-off filter | 45 mL acetonitrile (MeCN) + 5 mL trolamine (TEOA) + CO ₂ | CO: 298 | 51 |
| ZnM-LDH (M = Ti ⁴⁺ , Ga ³⁺ , Al ³⁺) | M | M | 300 W Xe lamp | 0.1 mL H ₂ O + 0.08 MPa CO ₂ | CH ₄ : 1.2 (68% M = Ti) (90% M = Al), CO: 1.6 (78% M = Ga) | 56 |
| CA@PCN-222 | Zr ^{III} -cluster | Zr ^{III} -cluster | 300 W Xe lamp (800 nm > λ > 400 nm) | 60 mL mixed solution (MeCN/TEOA = 30/1) + CO ₂ | HCOO ⁻ : 281.6 | 59 |
| UiO-Co-N ₃ | Co-N ₃ | Co-N ₃ | 300 W Xe lamp ($\lambda \geq 420$ nm) | 20 mL MeCN + 30 mg [Ru(bpy) ₃]Cl ₂ · 6H ₂ O + 0.025 M 1,3-dimethyl-1,3-dihydro-2-phenyl-2H-benzimidazole (BIH) + CO ₂ | CO: 179.3 (99.3%) | 61 |
| Incorporating Cu sites into the connected nodes of defective UiO-66-NH ₂ | NH ₂ -Cu-NH ₂ | NH ₂ -Cu-NH ₂ | 300 W Xe lamp ($\lambda > 420$ nm) | 2 mL H ₂ O + 6 mL N,N'-dimethylformamide (DMF) + CO ₂ | CH ₃ COCH ₃ : 70.9 (97%) | 62 |
| 2,2'-Bipyridine-based COF bearing non-noble single Cu sites | Cu ²⁺ sites | Cu ²⁺ sites | 300 W Xe lamp ($\lambda > 420$ nm) | 10 mL DMF or H ₂ O + 1 mL triethylamine + CO ₂ | CH ₄ : 17.5; CO: 1.6 (H ₂ O), CO: 10.2 (100%; DMF), CO: 22.5 (66.4%); DMF/H ₂ O = 50% | 63 |
| Cu-COF | Cu-O/N sites | Cu-O/N sites | 300 W Xe lamp ($\lambda > 420$ nm) | 12 mL mixed solution + 600 torr CO ₂ , MeCN/H ₂ O/TEOA (8 mL/2 mL/2 mL) | CO: 206 (94%) | 64 |
| Co-2,3-DHTA-COF | Co-O ₄ sites | Co-O ₄ sites | 300 W Xe lamp ($\lambda > 420$ nm) | 46 mL mixed solution + 10 mg [Ru(bpy) ₃]Cl ₂ · 6H ₂ O + 1 atm CO ₂ , MeCN/H ₂ O/TEOA (32 mL/8 mL/6 mL) | CO: 18 000 (95.7%) | 65 |
| Mo-COF | MoN ₂ sites | MoN ₂ sites | 300 W Xe lamp ($\lambda \geq 420$ nm) | 5 mL H ₂ O + 1 mL CO ₂ | CO: 6.19, C ₂ H ₄ : 3.57, CH ₄ : 1.08 | 66 |
| O/La-CN | La-N charge-transfer bridge | La-N charge-transfer bridge | Xe lamp | 12 mL mixed solution + 1 atm CO ₂ , MeCN/H ₂ O/TEOA (6 mL/4 mL/2 mL) | CO: 92 (80.3%) | 67 |
| Cu ₁ @BiOBr [Co ₃ O]ClO ₄ | Isolated Cu sites Co(II) catalytic center | Isolated Cu sites Co(II) catalytic center | 300 W Xe lamp 300 W Xe lamp ($\lambda > 420$ nm) | 5 mL H ₂ O + 4 MPa CO ₂ 5 mL mixed solution + [Ru(bpy) ₃]Cl ₂ · 6H ₂ O + BIH + CO ₂ MeCN/H ₂ O (4 mL/1 mL) | CH ₃ OH: 627.66 (86.6%) CO: 88.14% \pm 2.09% | 68 72 |
| CuNi-L ² | Active Ni ^{II} site | Active Ni ^{II} site | LED light ($\lambda > 420$ nm) | 25 mL mixed solution + [Ru(bpy) ₃]Cl ₂ · 6H ₂ O (0.85 mmol L ⁻¹) + Triisopropanolamine (TIPA) 0.8 mol L ⁻¹ + CO ₂ , MeCN/H ₂ O (20 mL/5 mL) | CO: (93.5%) | 73 |
| Cu single atoms on the nitrogen-doped carbon anchored on TiO ₂ | Cu SAS | Cu SAS | 300 W Xe lamp | H ₂ O vapor + CO ₂ | CO: 65.8 | 77 |
| 2Re-In ₂ O ₃ | O _{def} | O _{def} | 300 W Xe lamp | 100 mL H ₂ O + 1.01 bar CO ₂ | CH ₃ OH: 265.6 (100%) | 78 |
| Cu ₁ /TiO ₂ | Cu ₁ -O ₂₊₁ | Cu ₁ -O ₂₊₁ | Xe lamp | 20 mL H ₂ O + TEOA + CO ₂ | C ₂ H ₄ : 60.4 (75.2%) | 79 |
| MIL-88B-NS40 | Fe-N coordinated sites/uncoordinated S | Fe-N coordinated sites/uncoordinated S | 300 W Xe lamp ($\lambda > 420$ nm) | 2 mL H ₂ O + CO ₂ | C ₂ H ₄ : 17.7 | 80 |
| B-Ni ₁ /WO _{2.72} | Ni site | Ni site | 300 W Xe lamp ($\lambda > 420$ nm) | 6 mL mixed solution + 15 mg [Ru(bpy) ₃]Cl ₂ · 6H ₂ O + CO ₂ , MeCN/H ₂ O/TEOA (3 mL/2 mL/1 mL) | CO: 80 500 (98.7%) | 82 |
| Isolated Mn atoms over the multi-edged TiO ₂ nano-pompons | Mn atoms | Mn atoms | 300 W Xe lamp ($\lambda > 420$ nm) | 6 mL mixed solution + 10 mg [Ru(bpy) ₃]Cl ₂ · 6H ₂ O + 1 atm CO ₂ , MeCN/H ₂ O/TEOA (3 mL/2 mL/1 mL) | CO: 80 510, H ₂ : 23 070 | 83 |
| In-bonded N-atom (In ^{δ+} -N _i) in the (002) crystal planes of g-C ₃ N ₄ | In ^{δ+} -N _i | In ^{δ+} -N _i | 300 W Xe lamp | 400 μ L H ₂ O + CO ₂ | CO: 398.87 | 84 |



Table 1 (Contd.)

| Catalyst | Reactive sites | Light source | Reaction condition | Performance ($\mu\text{mol g}^{-1} \text{h}^{-1}$) | Ref. |
|---|--|--|---|--|----------|
| CuACs/PCN 3Er-ZnIn ₂ S ₄ | Cu-N ₃ sites doped P Er | 300 W Xe lamp | 5 mL TEOA + [Ru(bpy) ₃]Cl ₂ ·6H ₂ O + 45 mL H ₂ O + CO ₂ | C ₂ H ₄ : 10.17 (53.2%), CH ₄ : 9.55 | 85 |
| | | 300 W Xe lamp ($\lambda \geq 420$ nm) | TEOA + 100 mL H ₂ O + 80 kPa CO ₂ | CH ₄ : 6.68 (>90%) | 86 |
| Cu ₁ N ₃ @PCN Ag ₁ @PCNT | Different coordination structures Cu-atom Ag-N ₃ , Ag single atoms | 300 W Xe lamp ($\lambda > 420$ nm) | 1 mL H ₂ O + CO ₂ | CO: 49.8 | 87 |
| | | 300 W Xe lamp AM 1.5 cut-off filter | 3 mL H ₂ O + 70 kPa CO ₂ | CO: 160 (>94%) | 88 |
| Ultra-high Pr loading CN MCOF-Ti ₆ Cu ₃ | Pr ₁ -N ₄ O ₂ sites Cu cluster | 300 W Xe lamp | 1.0 mL H ₂ O + 4.0 mL CO ₂ | CH ₃ OH: 511.1 | 89 |
| | | Xe lamp AM 1.5 cut-off filter | 30 mL H ₂ O + CO ₂ | HCOOH: 169.8 | 90 |
| Dual MAS Mn ₁ Co ₁ /CN | Two compatible active centers of Mn and Co | 300 W Xe lamp ($\lambda > 400$ nm) | 2 mL H ₂ O + 80 kPa CO ₂ | CO: 47 | 17 |
| | | 300 W Xe lamp | 12.5 mL MeCN + 2.5 mL H ₂ O + 1 atm CO ₂ | C ₂ H ₄ : 7.6, C ₃ H ₈ : 13.8, CO: 18.6 | 46 |
| Cu-Ti-V ₂ O ₇ /Ti _{0.91} O ₂ -SL CuInP ₂ S ₆ monolayer | Cu-Ti-V ₂ O ₇ unit Cu-In dual site | 300 W Xe lamp AM 1.5 cut-off filter | 0.4 mL H ₂ O + CO ₂ | C ₂ H ₄ : 20.89 (56.4%), CO: 8.59, CH ₄ : 6.22 | 55 |
| | | 300 W Xe lamp | 10 mL mixed solution + 0.005 mmol [Ru(bpy) ₃] Cl ₂ ·6H ₂ O + 1.8 bar CO ₂ MeCN/H ₂ O/TEOA (6 mL/2 mL/ 2 mL) | CH ₄ : 217 (78.9%) | 57 |
| V into NiAl-LDH | V; lower-valence Ni | 300 W Xe lamp ($\lambda > 400$ nm) | 500 μL H ₂ O + 70–80 kPa CO ₂ | CO: 27.3 | 69 |
| Dispersed Co-Ru bimetal into conjugated porous carbon nitride polymer | Co sites; Ru sites | 300 W Xe lamp | 9 mL NaHCO ₃ (3 M) + 1 mL TEOA + CO ₂ | CH ₄ : 154 (95%), CO: 2, H ₂ : 6 | 70 |
| Ru Cu single atom incorporated into polymeric carbon nitride | Ru-N ₄ sites, Cu-N ₃ sites | 300 W Xe lamp | 5 mL mixed solution + 1 atm CO ₂ MeCN/TEOA (2.5 mL/ C ₂ H ₄ : 73.2 | | 74 |
| Re-bpy/PTF(Cu) | Re-bpy sites; Cu single sites in PTF(Cu) | 300 W Xe lamp (1100 nm > λ > 2.5 mL) 400 nm) | | | |
| Cu-N ₂ -V LaNi-Phen/COF-5 | Cu ⁺ /Cu ²⁺ Optically active (La site) catalytically active (Ni site) | 300 W Xe lamp | 21 mL DMF + 3 mL H ₂ O + 0.8 MPa CO ₂ | C ₂ H ₅ OH: 69.8 | 81 |
| | | 300 W Xe lamp | 10 mM BIH + 48 mL MeCN + 2 mL H ₂ O + 80 kPa CO ₂ | CO: 605.8 (98.2%) | 91 |
| CuIn ₅ S ₈ | Cu-In dual sites | 300 W Xe lamp ($\lambda > 400$ nm) | 2 mL H ₂ O + 0.1 atm CO ₂ | CH ₄ : 8.7 | 92 |
| | | 300 W Xe lamp | 5 mL H ₂ O or 5 mL 0.2% methanol aqueous solution was injected + CO ₂ | CH ₄ : 3.6 | 93 |
| Ag ₂ Cu ₂ O ₃ | Cu-Ag Lewis acid-base dual sites | Xe lamp (320 nm < λ < 780 nm) | H ₂ O + CO ₂ | CH ₄ : 35.49 (91.3%) | 94 |
| In/TiO ₂ -Vo | Vo-regulated In-Ti dual sites | 300 W Xe lamp ($\lambda > 400$ nm) | CO ₂ | CO: 64.1 $\mu\text{mol g}^{-1}$, CH ₄ : 7.7 $\mu\text{mol g}^{-1}$ | 95 |
| Au/Co dual single atom loaded Cds NPs | Asymmetric Zn-O-Ge sites | Xe lamp light | 12 mL H ₂ O + 0.03 vol% CO ₂ /Ar gas mixture | CH ₃ COOH: 12.7 (29.95%) | 96 |
| Vo-rich Zn ₂ GeO ₄ nanobelts | Au-O-Ce sites In-Cu dual sites | 300 W Xe lamp 300 W Xe lamp | 5 mL H ₂ O + 80 kPa CO ₂ 24 mL DMF/H ₂ O (12.5 vol% H ₂ O) + 0.8 MPa CO ₂ 1.0 mL H ₂ O + (CO ₂ -1%, N ₂ -99%) | CO: 11.07, C ₂ H ₆ : 11.07 (65.3%) C ₂ H ₅ OH: 28.5 (92%) | 97 98 |
| InCu/PCN | | | | | 99 |

Table 1 (Contd.)

| Catalyst | Reactive sites | Light source | Reaction condition | Performance ($\mu\text{mol g}^{-1} \text{h}^{-1}$) | Ref. |
|--|---|--|---|--|------|
| Bi_2WO_6 nanosheets with Vo anchoring Au and Cu dual single atoms | Au–Cu dual-single-atom sites; Vo | 300 W Xe lamp (780 nm > λ > 320 nm) | 15 mL H_2O + 0.5 MPa CO_2 | Total amount of production (CO , CH_4 , C_2H_4 , C_3H_6): 83.9 | 100 |
| 2% Pd–Cu/ TiO_2 | Pd–Cu; Vo | 300 W Xe lamp | 50 mL H_2O (0.1 M Na_2SO_3 + 0.2 M C_6OH) + CO_2 | CH_3OH : 71.84 (91.71) | 101 |
| Single atoms of Ni/Co loaded on TiO_2 | Ni/Co single atoms | 300 W Xe lamp | 1 mL H_2O + CO_2 | CH_3COOH : 22.6, 71% | 102 |
| Incorporated the redox-active $\text{Co}^{2+}/\text{Ni}^{2+}$ centers into the chemically stable layered lead iodide hybrids | $\text{Co}^{2+}/\text{Ni}^{2+}$ –O–Pb bimetallic catalytic sites | AM 1.5 G filter | | $\text{C}_2\text{H}_5\text{OH}$: 24.9–31.4, 89.5–93.6% | 102 |
| $g\text{-C}_3\text{N}_4/\text{UiO-66}(\text{Zr}/\text{Ce})$ | N–Zr/Ce–O | 300 W Xe lamp | 15 mL MeCN + 15 mL H_2O + 101 kPa CO_2 | CH_3OH : 54.71, $\text{C}_2\text{H}_5\text{OH}$: 38.10 | 103 |
| Cu–CuTCPP/ $g\text{-C}_3\text{N}_4$ | Cu^{1+6} | 300 W Xe lamp (800 nm > λ > 360 nm) | 400 μL H_2O + 200 μL TEA + 0.1 MPa CO_2 | CO: 12.3, CH_4 : 11.6, C_2H_6 : 18.5 | 104 |
| MAS combined P and Cu dual sites anchored on graphitic carbon nitride | P–N and Cu–N ₄ dual sites | 300 W Xe lamp | 3 mL TEOA + H_2O + 0.65 atm CO_2 | C_2H_6 : 616.6 | 31 |
| 1% Ru– TiO_{2-x} | Ru; Vo | 300 W Xe lamp | 0.14 g NaHCO_3 + N_2 + H_2O + H_2SO_4 (2 M) | CH_4 : 31.63 (90.93%) | 45 |
| A series of metastable WO_3 photocatalysts with the coexistence of S doping and Vo | W–S–W bridge; Vo | 300 W Xe lamp | 0.4 mL H_2O + CO_2 | C_2H_4 : 224.278, 87.6% | 47 |
| Au atoms to ultrathin ZnIn_2S_4 nanosheets with Vs | $\text{Au}_1\text{-S}_2$ | 300 W Xe lamp (λ > 420 nm) | 5 mL mixed solution + 10 mg $[\text{Ru}(\text{bpy})_3\text{Cl}_2 \cdot 6\text{H}_2\text{O} + 1 \text{ CH}_4$: 275 (77%) atm CO_2 , $\text{MeCN}/\text{H}_2\text{O}/\text{TEOA}$ (3 mL/1 mL/1 mL) | CH_4 : 44.3 (73%) | 52 |
| Vs–AgInP ₂ S ₆ single atomic layer | Ag atoms; Vs | 300 W Xe lamp | 0.4 mL H_2O + CO_2 | CO: 40.02 (82.9%) | 105 |
| Mn dopants and Vo were engineered in Zn_2GeO_4 nanorods | Mn dopants and Vo | 300 W Xe lamp | 1 mL H_2O + CO_2 | | 106 |
| $\text{Cu}_1/\text{N}_{2\text{C}}\text{V-CN}$ | Cu single atoms; N _{2C} vacancies | 300 W Xe lamp AM 1.5 cut-off filter | 200 μL H_2O + 105 kPa CO_2 | CO: 11.12 | 107 |
| $\text{CuGaS}_2/\text{Ga}_2\text{S}_3$ containing Vs | Cu–Ga metallic bond | 300 W Xe lamp (λ > 420 nm) | 3 mL H_2O + TEOA + 70 kPa CO_2 | C_2H_4 : 335.67 (93.87%) | 108 |
| $\text{Cu}_{1.95}\text{S}_{1-x}$ | Dual Cu and Vs | 300 W Xe lamp AM 1.5 cut-off filter | 1 atm CO_2 | CH_4 : 12.42 | 109 |
| MAS synergizing with nanoparticles | Cu nanoparticles; Ni single-atom sites; asymmetric Ni–N ₄ sites | 300 W Xe lamp (λ > 420 nm) | 95 mL H_2O + 5 mL TEOA + 100 kPa CO_2 | CH_4 : 35.245, CO: 32.067, C_3H_6 : 25.328 | 110 |
| $\text{Co}_1\text{Ag}_{(1-n)}\text{PCN}$ | Co–N ₆ –P bonds, Ag–N ₂ C ₂ SA sites, Ag NPs | 300 W Xe lamp | 6 mL CH_3CN + 4 mL H_2O + 80 kPa CO_2 | CO: 46.82 (70.1%) | 111 |
| Cu single atoms and nanoclusters supported on defective TiO_2 | Cu SAs, Cu NCs | 300 W Xe lamp | 100 μL H_2O + CO_2 | CH_4 : 19.63 (98%) | 112 |
| single Pd atoms and Pd nanoparticles on graphitic carbon nitride | Pd ₁ sites; Pd _{NPS} sites | Xe lamp | 10 mL H_2O + 1 atm CO_2 | CH_4 : 20.3 (97.8%) | 113 |
| MAS within heterostructure $g\text{-C}_3\text{N}_4/\text{CoCo-LDH}$ | Co–N ₂ bonds | 300 W Xe lamp | 3 mL H_2O + 1 atm CO_2 | CO: 71.39 | 58 |
| $\text{CuO}/\text{Cu}_2\text{V}_2\text{O}_7$ | Two metal atomic sites of Cu and V | 300 W Xe lamp | 20 mL TEOA + 80 mL H_2O + 1.01 bar CO_2 | CO: 118, C_2H_4 : 29.57 | 114 |
| 2D/2D Ni-doped $\text{CsPbBr}_3/\text{Bi}_3\text{O}_4\text{Br}$ scheme heterojunction | Ni ²⁺ | 300 W Xe lamp | 2 mL H_2O + 101 kPa CO_2 | CO: 96.89 (98.2%) | 115 |
| Co-TCPP/ $\text{Bi}_3\text{O}_4\text{Br}$ | Bi–O bridge bond; Co atoms | 300 W Xe lamp | 50 mL H_2O + 0.08 MPa CO_2 | CO: 71.3 | 115 |





Table 1 (Contd.)

| Catalyst | Reactive sites | Light source | Reaction condition | Performance ($\mu\text{mol g}^{-1} \text{h}^{-1}$) | Ref. |
|---|---|---|---|---|------------|
| Cu-SAEB | N-Cu ₁ -S single-atom electron bridge | 300 W Xe lamp | 0.1 mL H ₂ O + CO ₂ | CO: 236.0, O ₂ : 120.1 | 116 |
| In ₂ O ₃ /CdSe-diethylenetriamine 2D/0D g-C ₃ N ₄ /Cu ₂ SnS ₃ | In-O-Cd bonds; Vo Cu-C and Cu-N dual chemical bond; Cu sites | 300 W Xe lamp 100 W Xe lamp AM 1.5 filter | 120 mg NaHCO ₃ + 0.5 mL H ₂ SO ₄ H ₂ O + CO ₂ | CO: 70.08, CH ₄ : 27.92 CO: 18.2 | 117 118 |
| NiAl-Fe-TCPP | Fe; Ni | 300 W Xe lamp | 0.005 mmol [Ru(byp) ₃]Cl ₂ · 6H ₂ O + 10 mL mixed solution + 1.8 bar CO ₂ /MeCN/H ₂ O/TEOA (6 mL/2 mL/2 mL) | C ₂ H ₄ : 2470 | 119 |
| r-In ₂ O ₃ /InP | O-In-P polarized sites | 300 W Xe lamp ($\lambda > 420$ nm) | 100 mL H ₂ O + 80 kPa CO ₂ | CH ₃ COOH: 9.67 (96.1%) | 120 |
| CdS:Dy ³⁺ /g-C ₃ N ₄ | Dy ³⁺ single atom | 300 W Xe lamp ($\lambda > 400$ nm) | 4 mL H ₂ O + CO ₂ | CH ₄ : 8.06 | 121 |
| Bi NCS/Bi ₂ O ₃ | Bi ⁰ of Bi NCS | 300 W Xe lamp ($\lambda > 420$ nm) | 1 mL H ₂ O + 0.08 MPa CO ₂ | CH ₄ : 7.45 (94.8%) | 122 |
| CsCuCl ₃ /Cu NCS | Cu NCS | 150 W Xe lamp AM 1.5 cut-off filter | 4 mL ethyl acetate (EA) + 1 mL propan-2-ol (IPA) + CO ₂ CH ₄ : 7.2 (92.7%) | | 123 |
| Ultrathin Bi ₁₂ O ₁₇ Cl ₂ nanosheets Bi-BiOCl plasmonic nanoparticles decorated TiO ₂ nanosheets | Vo; Bi clusters Bi | 300 W Xe lamp 300 W Xe lamp AM 1.5 cut-off filter | 50 mL H ₂ O + 0.08 MPa CO ₂ 5 mL 0.2 M NaHCO ₃ + CO ₂ | CO: 64.3 CH ₃ OH: 235.78 ($\approx 90\%$) | 124 125 |
| Au/TiO ₂ /W ₁₈ O ₄₉ | Au-O-Ti, W-O-Ti | 300 W Xe lamp ($\lambda > 420$ nm) | 0.1 mL H ₂ O + CO ₂ | CH ₄ : 35.55, CO: 2.57, CH ₄ (93.3%) | 126 |
| PtAg-2/HNb ₃ O ₈ | Pt-Ag alloy (7 : 43 Pt-Ag molar ratio) | 300 W Xe lamp (320 nm < λ < 780 nm) | 2 mL H ₂ O + 0.09 MPa CO ₂ | CH ₄ : 93.6 (74.3%) | 127 |
| PtCu/TiO ₂ | Pt/Cu alloy (0.4 : 0.6) | 300 W Xe lamp (300 nm < λ < 400 nm) | Water vapor + CO ₂ | CH ₄ : 100% | 128 |
| Cu-Ag/TiO ₂ | Cu-Ag alloy (0.8 : 0.2) | 300 W Xe lamp AM 1.5 cut-off filter | 150 mL H ₂ O + 90 kPa CO ₂ | C ₂ H ₄ : 1110.6 | 129 |
| AuIr with InGaN nanowires on silicon | Au ₃ Ir ₁ alloy (0.44 : 0.56) | 300 W Xe lamp | 30 mL H ₂ O + 2 atm CO ₂ | C ₂ H ₆ : 58 800, CH ₄ : 125 400, H ₂ : 735 600, CO: 127 800 | 130 |
| Au/TZO | Au nanoparticles | 300 W Xe lamp AM 1.5 G filter | 20 mL mixed solution + 1 atm CO ₂ MeCN/H ₂ O/TEOA (16 mL/2 mL/2 mL) | H ₂ : 271.6, CO: 260.6, C ₂ H ₄ : 6.80, C ₂ H ₆ : 4.05 | 131 |
| Bi nanoparticles grown on the Bi ₂ MoO ₆ with Vo | Bi nanoparticles Vo | Xe lamp | 0.42 g NaHCO ₃ + 30 mL H ₂ O + CO ₂ | C ₂ H ₅ OH: 17.93 (92%) | 132 |

CO₂, where the strong hybridization of the Cu 3d and CO₂-O 2p orbitals facilitated the transfer of electrons from the Cu single atoms to CO₂, effectively optimizing the rate-limiting step (CO₂* → COOH*). Moreover, single MAS also improved the selectivity of the liquid product of the photocatalytic CO₂ reduction. The atomically dispersed rhenium (Re) in In₂O₃ changed the product from CO on pure In₂O₃ to CH₃OH on 2Re-In₂O₃.⁷⁸ DFT calculations disclosed that the Re site promoted the H₂O dissociation to form sufficient H atoms for CO₂ reduction. Critically, CO preferred to be hydrogenated into CHO instead of desorption due to the strong binding between CO and Re₁-In₂O₃(111). Through multi-step hydrogenation, CHO was eventually converted to CH₃OH with high selectivity.

Photocatalytic CO₂ conversion mainly involves C=O bond cleavage and C-H bond formation, accompanied by the challenging C-C coupling toward the generation of C₂₊ products. The MAS could reduce electrostatic repulsion between the C₁ intermediates, promote C-C coupling, and thus lead to the highly selective formation of the C₂₊ product. The photo-generated electron transition from TiO₂ to atomically dispersed Cu atoms rearranged the energy levels of the Cu 3d orbitals.⁷⁹ Consequently, the initial four-coordinated Cu₁-O₄ was distorted into a Cu₁-O₂₊₁ structure (twofold normal Cu-O coordination and one stretched Cu-O coordination), which could be reversibly recovered after removing the synergistic light field. The photoinduced metastable intermediate of Cu₁-O₂₊₁ delivered an C₂H₄ yield rate of 60.4 μmol gcat⁻¹ h⁻¹. The energy barrier of the first protonation step from CO₂ to *COOH showed an obvious decline over Cu₁-O₂₊₁, indicating the stronger activation capability of the metastable asymmetrical structure to reactants than that of Cu₁-O₄. *CO molecules adsorbed more strongly on the Cu₁-O₂₊₁ (-1.49 eV) surface than on the Cu₁-O₄ (-0.44 eV) surface, leading to subsequent hydrogenation rather than desorption. It was noteworthy that, in contrast to Cu₁-O₄, Cu₁-O₂₊₁ promoted C-C coupling and further formation of C-C bonds, thus facilitating the generation of C₂H₄. Furthermore, N,S-codoped Fe-MOF MIL-88B with a well-defined bipyramidal hexagonal prism shape was designed.⁸⁰ The synergistic effect of the Fe-N coordinated sites and reasonable defects from uncoordinated S increased the electron density disorder around Fe, accelerated the migration of photo-generated carriers, benefited electron storage, and effectively promoted the formation of C-C coupling intermediates for C₂H₄. For liquid products, the carbon nitride-supported Cu single-atom catalyst with a defective low-coordination Cu-N₂ motif (Cu-N₂-V) exhibited superior photocatalytic activity for CO₂ reduction to ethanol relative to Cu-N₃ and Cu-N₄.⁸¹ In particular, Cu in Cu-N₂-V existed in both Cu⁺ and Cu²⁺ valence states. On the one hand, the Cu⁺ sites benefited CO₂ activation. On the other hand, the coexistence of Cu⁺/Cu²⁺ sites contributed to the strong adsorption of *CO and subsequent *CO-*CO dimerization. Finally, ethanol was ultimately produced from *CO-*CO, which underwent a series of hydrogenation processes.

The d-band center tuning strategy influences the carrier transportation and the adsorption of the reactant and intermediate to promote photocatalytic CO₂ conversion, which can

be achieved by incorporating MAS. Bulk doping of single Ni atoms in WO_{2.72} (B-Ni₁/WO_{2.72}) displayed superior solar-driven CO₂ reduction performance to surface anchoring of single Ni atoms on WO_{2.72} (S-Ni₁/WO_{2.72}).⁸² The introduction of Ni atoms led to an upward shift of the d-band center of W atoms in the WO_{2.72} host structure due to the overlapping orbital hybridization. Critically, the d-band center of W in B-Ni₁/WO_{2.72} shifted upward to a greater extent relative to S-Ni₁/WO_{2.72}. Therefore, the Ni atoms in B-Ni₁/WO_{2.72} exhibited stronger electronic interactions with the WO_{2.72} host, facilitating the formation of charge-transfer channels that enabled the rapid transfer of photogenerated electrons to the surface Ni atoms. Moreover, the free energies of *CO₂, *COOH, and *CO intermediates of B-Ni₁/WO_{2.72} were integrally decreased compared to those on S-Ni₁/WO_{2.72}, benefiting the conversion of CO₂ to CO. Analogously, the decoration of isolated Mn atoms over the multi-edged TiO₂ nano-pompons shifted the d-band center upwards and pushed the antibonding orbital closer to the Fermi level, thus facilitating CO₂ adsorption.⁸³ The Mn site acted as an active center for CO₂ activation, and significantly reduced the formation energy barriers of *COOH to accelerate the decisive step of the reaction.

Besides in-plane regulation, MAS can realize interlayer-spacing adjustment, which may significantly influence the carrier transport of the bulk-catalyst, thereby affecting CO₂ photoreduction. Single-atom In-bonded N-atom (In^{δ+}-N₄) in the (002) crystal planes of g-C₃N₄ reduced the (002) interplanar spacing of g-C₃N₄, benefiting the separation of bulk carriers.⁸⁴ More charges were transferred to the adsorbed CO₂ molecule from the In^{δ+}-N₄ active center (0.116 eV) compared to the bare C₃N₄ site (0.006 eV), which was favorable for CO₂ adsorption. Moreover, the In^{δ+}-N₄-led CO₂ hydrogenation to *COOH was downhill by -0.114 eV and evidently surpassed the uphill step by 2.09 eV on the bare C₃N₄, which optimized the reaction path.

3.2 Dual MAS

The precise construction of photocatalysts with dual MAS to achieve the simultaneous fostering of light absorption and catalytic activity is a formidable challenge. The bifunctional LaNi sites within COF were synthesized by electrostatically driven self-assembly approach.⁹¹ The La-Ni dual MAS accelerated the dynamic behavior of the photogenerated charge carriers, comprising photoelectron transfer from La-Phen to the COF-5 colloid and subsequent electron injection into Ni-Phen for the CO₂ reduction process. In addition, the bimetallic LaNi coordination facilitated the generation of abundant *COOH groups, and effectively decreased the activation barrier of CO₂ transformation. Moreover, the CO desorption was thermodynamically preferred over CHO* formation, with an energy barrier of 0.72 eV *versus* 1.02 eV, resulting in high CO selectivity.

Precise control of the formation of Metal₁···C=O···Metal₂ (M₁···C=O···M₂) intermediates at the photocatalyst interface is one of the critical steps in the formation of hydrocarbons. This is due to the fact that the energy required for simultaneous cleavage of the M₁···O and M₂···C bonds is much greater than that required for C-O bond breaking (Fig. 9a).⁹² Ag₂Cu₂O₃



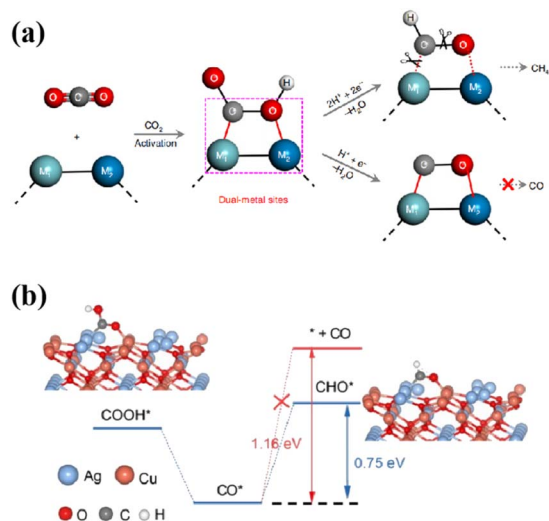


Fig. 9 (a) CO_2 photoreduction into fuels such as CH_4 and CO through the use of dual-metal-site catalytic systems (M represents the metal site, ' $\text{H}^+ + \text{e}^-$ ' refers to the proton coupled electron transfer process and ' $-\text{H}_2\text{O}$ ' means the desorption of H_2O molecules after the intermediates react with the proton–electron pair). This figure has been reproduced from ref. 92 with permission from Springer Nature, copyright 2019. (b) The rate-determined step of photoreduction of CO_2 into CH_4 over $\text{Ag}_2\text{Cu}_2\text{O}_3$ nanowires. This figure has been reproduced from ref. 93 with permission from Wiley-VCH, copyright 2023.

nanowires with abundant Cu–Ag Lewis acid–base dual sites on the preferentially exposed (110) surface were utilized as a model catalyst to achieve 100% selectivity in the photogeneration of CH_4 from CO_2 .⁹³ The $\text{Cu}\cdots\text{Ag}$ Lewis acid–base dual sites on $\text{Ag}_2\text{Cu}_2\text{O}_3$ (110) regulated the $\text{M}_1\cdots\text{C}=\text{O}\cdots\text{M}_2$ intermediate formation, converting CO_2 into hydrocarbons. The rate-determining step with a corresponding Gibbs free energy ($\Delta G(\text{CHO}^*)$) of 0.75 eV led to greater feasibility in CO^* forming CHO^* than desorbing from the catalyst surface (1.16 eV, Fig. 9b). Similarly, the highly stable Cu–C–O–In intermediate at the Cu–In dual sites of the sulfur-deficient CuIn_5S_8 converted the endoergic protonation step to an exoergic reaction process, changing the reaction pathway to form CH_4 instead of CO .⁹² Furthermore, the V_O -regulated In–Ti dual sites enabled the formation of a stable adsorption conformation of the In–C–O–Ti intermediate, leading to the highly selective reduction of CO_2 to CH_4 .⁹⁴

Catalysts containing dual MAS regulates the electron distribution by creating asymmetric atomic configurations, which significantly affects the photocatalytic performance, especially for multi-electron CO_2 reduction. The mechanism of reverse electron transfer over Au and Co bimetallic atom catalysts was reported.⁹⁵ Electrons were delocalized from Au and accumulated around the Co atoms, resulting in the electron-rich Co atoms adsorbing/activating CO_2 molecules readily, which significantly promoted photocatalytic CO_2 reduction. In this regard, the Au/Co double single-atom loaded CdS increased the yield of CO and CH_4 by nearly 2800% and 700%, respectively, compared to CdS alone. In addition, the disparate electron distributions and valence states of two distinct metal atoms

could endow significantly different charge distributions of the neighboring C_1 intermediates to effectively suppress the electrostatic repulsion. The asymmetric Zn–O–Ge triatomic sites in the Vo-rich Zn_2GeO_4 nanobelts induced distinct charge distributions of neighboring C_1 intermediates, which facilitated the C–C coupling with a high CO_2 -to- CH_3COOH conversion rate of 29.95%.⁹⁶ Under similar mechanisms, incorporating redox-active $\text{Co}^{2+}/\text{Ni}^{2+}$ cations (TM) into layered lead iodide hybrids (TJU-39(Pb)) achieved efficient photocatalytic CO_2 -to- $\text{C}_2\text{H}_5\text{OH}$ conversion (yield of 24.9–31.4 $\mu\text{mol g}^{-1} \text{h}^{-1}$, selectivity exceeding 90%).¹⁰² It was experimentally demonstrated that the interlayer TMs were delocalized to the lead iodide layers to construct TM–O–Pd sites with substantial asymmetric charge distribution, which reduced the reaction barrier for C–C coupling. Specifically, the two-electron reduction of CO_2 to CO^* occurred simultaneously at the charge-enriched Pb^{2+} sites and the Ni^{2+} site, which subsequently underwent C–C coupling to form $\text{OC}-\text{CO}^*$ intermediates. The $\text{OC}-\text{CO}^*$ intermediate coupled multiple e^-/H^+ pairs, combining the dehydration process to finally yield $\text{C}_2\text{H}_5\text{OH}$.

From an overall reaction perspective, the CO_2 photoreduction contains oxidation and reduction half-reactions, involving multiple proton-coupled electron transfer processes. The MAS construction not only enhances CO_2 reduction, but also influences the corresponding oxidation half-reaction. The existence of an internal electric field pointing from the Ti cluster to the Cu cluster in $\text{MCOF-Ti}_6\text{Cu}_3$ facilitated carrier separation, leading to electron and hole transfer to the Cu cluster and Ti cluster, respectively.⁹⁰ Consequentially, electrons reaching the Cu cluster drove the reductive reactions, and the oxidative reaction proceeded at the Ti cluster. Analogously, two compatible active centers of Mn and Co were loaded onto carbon nitride ($\text{Mn}_1\text{Co}_1/\text{CN}$).¹⁷ The active center of Mn promoted H_2O oxidation by accumulating photogenerated holes, along with Co-facilitated CO_2 activation by increasing the bond length and bond angle of CO_2 molecules.

3.3 MAS combined with vacancies

Vacancies exhibit great influence on the properties of MAS. Vo-containing Co_3O_4 hollow nanoparticles loaded on a macroporous N-doped carbon framework realized the photoreduction of low-concentration CO_2 to CO .¹³³ Vo distorted the nearby Co–O bonds, broke the local structural symmetry of the Co–O–Co sites, and thus caused an asymmetric distribution of charge density compared with pristine Co_3O_4 . This asymmetrical active site with a polarized electronic structure endowed a stronger electrostatic interaction between the CO_2 molecule and Vo, which switched the CO_2 configuration from a single-site linear model to a multiple-sites bending one, therefore facilitating CO_2 activation. Moreover, the hydrogenation of adsorbed $^*\text{CO}_2$ proceeded smoothly on the Vo- Co_3O_4 surface, and the adsorption capacity of $^*\text{COOH}$ was obviously stronger than that of Co_3O_4 . Mn dopants and Vo were engineered in Zn_2GeO_4 nanorods (denoted as Mn-ZGO-Vo), which exhibited prominent photocatalytic CO_2 reduction performance.¹⁰⁵ The introduction of Vo in Mn-ZGO-Vo caused the charge accumulation on the Mn



atoms near Vo, certainly favoring the electron-rich Mn sites for CO₂ molecule capture. The lattice strain and ligand effects caused by Mn doping and Vo engineering elevated the d-band centers, endowing less filling of the antibonding states and hence stronger binding strength of CO₂. Moreover, the formation of COOH* on the Mn-ZGO-Vo slab changed from endothermic to exothermic, and the rate-limiting step was tuned to CO* formation with a lowest energy barrier among ZGO and Mn-ZGO. Precisely constructed Cu single-atom centers and two-coordinated N vacancies as dual active sites on carbon nitride (Cu₁/N₂CV-CN) achieved a high carbon-based selectivity of 98.50% for CO production.¹⁰⁶ The atomic Cu active sites promoted the chemisorption of CO₂ by changing the electronic structure of the surface. The N₂C vacancy became the active site for the adsorption of H₂O, which accelerated the dissociation of H₂O by reducing the dissociation energy barrier of H₂O from 2.59 eV to 1.68 eV. Moreover, the decrease in the rate-limiting step (the formation of COOH* species) by the dual active sites in Cu₁/N₂CV-CN led to a decent CO production rate of 11.12 μmol g⁻¹ h⁻¹.

The geometry of MAS regulated by vacancies ultimately affects the catalytic performance to generate C₂₊. Ultra-thin CuGaS₂/Ga₂S₃ containing Vs realized the selectivity of C₂H₄, reaching ≈ 93.87% with the yield of ≈ 335.67 μmol g⁻¹ h⁻¹.¹⁰⁷ Vs induced a highly delocalized electron distribution in the original region of S atoms, forming a Cu–Ga metallic bond. The upshift of the d-band center of Cu–Ga ions induced by Vs could not only enforce the adsorption ability for the intermediates of *CHOH*CO to initiate C–C coupling, but also accumulate electrons to drive the kinetic process of photocatalytic CO₂ reduction.

3.4 MAS synergizing with nanoparticles

The synergistic effect of MAS and nanoparticle accelerates the complex activation and hydrogenation process of photocatalysis. Introducing such a complex structure for simultaneous CO₂ reduction and H₂O dissociation is still a formidable challenge, and its underlying mechanism remains to be elucidated. The nitrogen-doped carbon anchoring with Cu nanoparticles and Ni single-atom sites (Ni₁Cu_{NP} N–C) were hybridized with CoAl-LDH (CA) for photocatalytic CO₂ reduction (CA/Ni₁Cu_{NP} N–C).¹⁰⁹ The photogenerated electrons of CoAl-LDH were transferred to N–C in the presence of the internal potential, and eventually accumulated on dispersed Ni single-atom sites. Meanwhile, the loading of Cu nanoparticles could significantly facilitate this charge transfer. The Ni center showed a high charge density, which facilitated reactant/intermediate adsorption and promoted catalytic reactions with multi-electron participation. Furthermore, the charge density around the electron-rich center Ni–N₄ showed an asymmetric distribution in the presence of Cu nanoparticles. This asymmetric active site was favorable for coupling adjacent *CO, thus promoting the generation of C₂ products. A cooperative catalyst containing Ag nanoparticles with adjacent atomic cobalt–silver dual-metal sites on P-doped carbon nitride (Co₁Ag_(1+n)-PCN) was reported for photocatalytic CO₂

reduction.¹¹⁰ The asymmetric Co–N₆–P sites coupled with Ag–N₂C₂ sites could serve as the charge transfer channel to facilitate the migration of electrons to the surface reaction sites, while Ag nanoparticles acted as the electron acceptor to enrich and separate photogenerated electrons. Moreover, the synergistic function of Ag nanoparticles with adjacent atomically dispersed Ag–N₂C₂ and Co–N₆–P single-atom sites promoted the adsorption of CO₂ molecules onto the photocatalyst surface, and facilitated the formation of CO₂* and COOH*.

3.5 MAS within a heterostructure

The construction of heterogeneous structures enhances light absorption and provides sufficient reaction sites.⁴⁴ In addition, the heterostructure can realize the spatial separation of the reduction and oxidation reaction sites, improving the utilization rate of the photogenerated carrier and preserving high-energy electrons and holes. MAS is conducive to the tight connection of heterogeneous structures and promotes the directional carrier transportation. The presence of Vo exposed Bi atoms on the Bi₃O₄Br surface, which formed an interfacial Bi–O bond by grafting the terminal O of the cobalt porphyrin (Co-TCPP).¹¹⁵ The Bi–O bond, as a charge-transfer bridge, promoted the extraction and transfer of photogenerated electrons from the external [Bi₃O₄] layers to Co-TCPP. This contributed an effective space charge separation and the slow recombination process on the μs–ms time scale of CoTCPP. MoS₂ decorated with Cu species (Cu₁/MS) was coated on the surface of MIL-125-NH₂ (MIL), which constructed a N–Cu₁–S single-atom electron bridge (denoted as Cu-SAEB).¹¹⁶ The Cu-SAEB achieved a Z-scheme charge-transfer mode between Cu₁/MS and MIL, thus prolonging the lifetimes of carriers with a strong redox potential. Benefiting from the strengthened contact interface of Cu-SAEB, the highly active and stable CO₂ reduction performance was achieved, with CO and O₂ formation rates of 236.0 and 120.1 μmol g⁻¹ h⁻¹, respectively. Similarly, an In–O–Cd bond-modulated S-scheme heterojunction of In₂O₃/CdSe-diethylenetriamine accelerated the photogenerated electron transfer.¹¹⁷ Combined with the electron capture effect of Vo in In₂O₃, the In–Vo–In–O–Cd structural units at the interface led to the extraction of electrons and the rapid transfer to the surface-active sites, improving the electronic coupling of CO₂.

The interface of the heterostructure could natively provide MAS for photocatalytic reactions. For example, the unique Cu–C and Cu–N dual chemical bond at the interface of the fabricated g-C₃N₄/Cu₂SnS₃ nanocomposite led to a superior CO formation rate from CO₂ photoreduction.¹¹⁸ The Z-scheme carrier conduction was highly activated due to the interfacial nitrogen vacancies *via* the Cu–C and Cu–N bonding for CO₂ reduction on the conduction band (CB) of Cu₂SnS₃ and water oxidation on the VB of g-C₃N₄. The more negative overall free energy of Cu sites relative to Sn and S implied that the CO₂ conversion reaction occurred mainly *via* effective dual bonds between Cu sites and the C and N elements in g-C₃N₄.¹¹⁸

Heterogeneous structures enriched with MAS can generate C₂₊ products. A novel supramolecular assembly of NiAl-Fe-TCPP obtained by intercalating iron porphyrin (Fe-TCPP) into



NiAl-layered double hydroxide (NiAl-LDH) exhibited superior catalytic performance of CO₂ photoreduction to derive C₂H₄ with high selectivity up to 93.4%.¹¹⁹ The strong host-guest interaction between LDH and Fe-TCPP led to the electron transfer from NiAl-LDH to Fe-TCPP. According to the *ex/in situ* XAS, the valence of Fe decreased along with the increase of Ni valence compared with that of Fe-TCPP and LDH, respectively. The low valence of Fe in NiAl-Fe-TCPP facilitated the CO* hydrogenation and coupling with CHO* to form COCHO*. Particularly, the CO₂ activation to CO was accomplished on NiAl-LDH, and then spilled to Fe-TCPP and coupled to generate COCHO*, which was further hydrogenated to produce C₂H₄. The O-In-P polarized sites at the r-In₂O₃/InP interface promoted C-C coupling with a productivity of 96.7 μmol g⁻¹ and selectivity >96% for CO₂ photoreduction to CH₃COOH.¹²⁰ The interfacial In atoms accumulated electrons and transferred electrons to CO₂, thus promoting CO₂ adsorption and activation. The quite different carbon Bader charges of OCCO* on r-In₂O₃/InP caused by the formation of rich O-In-P reactive sites at the interface alleviated dipole-dipole repulsion and promoted C-C coupling (Fig. 10a-c). Ultimately, the C-C coupling energy barrier of r-In₂O₃/InP (0.5461 eV) was lower than that of pure In₂O₃ (0.9446 eV), suggesting that the formation of heterostructures by modifying In₂O₃ with P favored the formation of C₂₊ products (Fig. 10d).

3.6 MAS as cocatalysts

The cocatalyst plays a crucial role in semiconductor-based photocatalysis, which is conducive to the migration of electrons or holes, and improves the utilization efficiency of the photogenerated carrier. Moreover, cocatalysts can reduce the activation energy and overpotential of the CO₂ conversion to speed up the surface reaction.⁴⁴ MAS used as cocatalysts can

effectively improve photocatalytic performance. Bi nanoclusters (NCs) were prepared *in situ* on Bi₂O₃ through dehalogenation of Bi₃O₄Br by regulating the pH value in the hydrothermal process.¹²² The construction of Bi sites on the basis of Bi₂O₃ could promote photogenerated charge transfer through the Schottky junction. Moreover, the change of the valence state of Bi regulated the type of active sites from O of the original Bi₂O₃ to Bi⁰ of the Bi NCs in Bi NCs/Bi₂O₃, thus regulating the path of CO₂ photoreduction. Thermodynamically, the *CO intermediate on the Bi site tended to hydrogenate to *CHO species, accompanied by a subsequent multi-step hydrogenation process that selectively generated CH₄ on Bi NCs/Bi₂O₃. The *CO desorption to form CO over Bi₂O₃ was spontaneous and exothermic, whereas the hydrogenation of *CO to form the *CHO species required overcoming a large energy barrier (2.29 eV), leading to CO being the only reduction product of Bi₂O₃. Similarly, the CsCuCl₃/Cu heterojunction synthesized *via* a simple acid-etching solution process exhibited high CH₄ selectivity.¹²³ The accumulating of charges at the contact interface between CsCuCl₃ and Cu nanocrystals formed a Schottky contact, facilitating the extraction of photoelectrons from CsCuCl₃ to Cu nanocrystals, thereby realizing the effective separation of photogenerated electron-hole pairs. Moreover, the Cu nanocrystals accelerated the photocatalytic CO₂ reduction toward CH₄ *via* manipulating the adsorption and activation of CO₂ and stabilizing the reaction intermediates.

The surface plasmon resonance of MAS plays a crucial role in the collection and conversion of solar energy by the strong local fields. The coexistences of Vo and Bi clusters generated *in situ* on ultrathin Bi₁₂O₁₇Cl₂ nanosheets contributed to the high efficiency of the CO₂-to-CO conversion.¹²⁴ The Bi clusters exhibited a plasmon effect that extended the light absorption and enabled more sunlight harvest. Furthermore, Bi clusters acted as hole trapping centres in synergy with Vo as electron trapping sites, leading to the spatial separation of photo-generated electron-hole pairs. As another example, the attachment of non-noble plasmonic Bi particles with BiOCl shells to self-assembled TiO₂ nanosheets created a transformative hybrid plasmonic nanostructure. Bi stabilized by the BiOCl shell generated robust localized surface plasmon resonances, inducing a local field enhancement of 7–9 times, thus enabling the efficient and selective CO₂-to-methanol conversion at the TiO₂-BiOCl heterointerfaces.¹²⁵ In addition, it is worth mentioning that the localized surface plasmon resonance effect of Bi nanoparticles could significantly improve the rate and selectivity of the C₂H₅OH generation.¹³² The high localized electron density and abundance of hot electrons in the active site drove the multi-electron reduction reaction, favoring the generation of C₂₊ products.

Plasmon resonance-mediated photocatalysis on precious metal surfaces (mainly Ag and Au) shows great potential for solar energy harvesting and conversion. For instance, plasmonic Au mediated the S-scheme charge transfer, and generated additional energetic hot electrons and holes to inject to the CB of ZnIn₂S₄ and VB of CuS, respectively, enabling a more thorough separation of carriers for CO₂ reduction and H₂O oxidation.¹³⁴ Moreover, a new idea of plasmonic active “hot

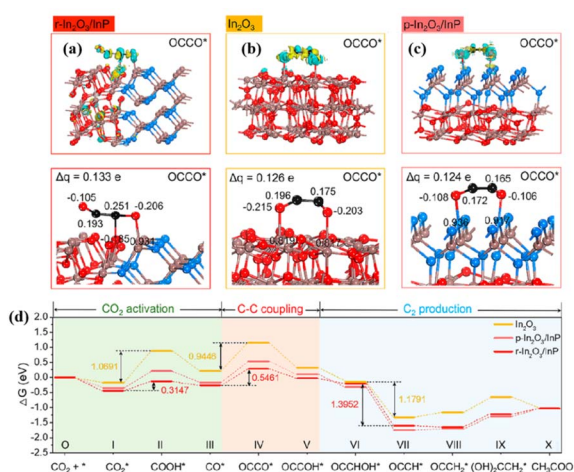


Fig. 10 Calculated electron density difference diagrams and the Bader charge values of (a) r-In₂O₃/InP, (b) In₂O₃, and (c) p-In₂O₃/InP with OCCO* absorbed. (d) Free energy diagrams for the reduction of CO₂ to CH₃COOH over r-In₂O₃/InP, In₂O₃, and p-In₂O₃/InP. These figures have been reproduced from ref. 120 with permission from American Chemical Society, copyright 2023.



spot"-confined photocatalysis was proposed to improve the photocatalytic CO₂ conversion. Specifically, tiny gaps (<10 nm) between the plasma nanostructures promoted plasma coupling between the nanostructures, resulting in the formation of classical "hot spots". The Au/TiO₂/W₁₈O₄₉ sandwich-like substructures with the short distance (<10 nm) between Au and adjacent W₁₈O₄₉ induced an intense plasmon-coupling to form the active "hot spots" in the substructures.¹²⁶ These active "hot spots" could gather the incident light to enhance "hot electron" generation and migration, and capture protons and *CO through the dual-hetero-active-sites (Au–O–Ti and W–O–Ti) at the Au/TiO₂/W₁₈O₄₉ interface, thus accelerating the protonation of *CO intermediates to derive CH₄.

Alloys as MAS enhance light absorption, inhibit charge recombination, and adsorb and activate reactants, thereby improving the selectivity of specific products. The PtAg alloy over HNb₃O₈ nanosheets trapped the electrons and improved the charge separation efficiency, mitigating the kinetical challenge of the eight-electron transfer process for CH₄.¹²⁷ In addition, the PtAg alloy acted as synergistic sites to reduce CO₂ to CO intermediates at the Ag site, which were then spilled over or sequentially adsorbed at neighboring Pt sites for further hydrogenation to CH₄. As another example, PtCu alloys with appropriate Pt/Cu ratios were deposited onto TiO₂ nanocrystals, which significantly improved CH₄ production with 100% selectivity.¹²⁸ The PtCu alloy effectively facilitated the separation/transfer of photogenerated charges, benefited the adsorption of CO₂, and promoted the formation and activation of intermediates (CO₂⁻, *COOH, *CO, and *CHO). The synergistic effect of PtCu lowered the activation energy barriers of *CO₂ and *CHO, inhibited the desorption of *CO, and ultimately optimized the efficiency and selectivity of CH₄.

The alloy MAS promotes the C–C coupling and desorption of *C₂ intermediates from the catalyst surface. Loading Cu–Ag alloy sub-nanoclusters (ASNCs) on TiO₂ for CO₂ photoreduction produced C₂H₄ with a record-high formation rate (1110.6 ± 82.5 μmol g⁻¹ h⁻¹).¹²⁹ The interaction between Cu and Ag in the Cu–Ag ASNCs promoted the C–C coupling of CH₂* at the Cu active site, which led to the spontaneous formation of *C₂H₄ from CH₂* on Cu–Ag alloy/TiO₂. In addition, the desorption energy of *C₂H₄ in the Cu–Ag alloy/TiO₂ was lower than that in Ag/TiO₂. This suggested that the interaction between Cu and Ag promoted the desorption of *C₂H₄, and thus the selective and efficient production of C₂H₄. Ag, in conjunction with Ir, achieved C–C coupling by inserting CO₂ into –CH₃, facilitating the formation of C₂*, during CO₂ photoreduction.¹³⁰ Specifically, the assembly of AuIr with InGa₃N nanowires on silicon achieved a C₂H₆ activity of 58.8 mmol g⁻¹ h⁻¹ with a turnover number of 54 595 over 60 h. The Ir sites in Au–Ir alloys increased CO₂ reduction activity by lowering the reaction energy of key elementary steps (for example, CO₂ to *COOH on pure Au and *CO to *CHO on Au₃Ir₁ alloy) and steered the selectivity from the dominant HER to C–C coupling. The insertion of CO₂ into *CH₃ toward *CH₃COO exhibited the lowest reaction energy compared with other C–C coupling forms (CH + *CH → *C₂H₂, *CH₂ + *CH₂ → *C₂H₄, *CH₃ + *CH₃ → C₂H₆(g) and CO₂

insertion into *CH₃ to *CH₃COO), revealing the possible mechanism of C–C coupling for C₂H₆ synthesis.

4 Identification the role of MAS in photocatalysis

With the growing development in nanoscale characterization, a variety of techniques have emerged to assess the role played by MAS in photocatalysis. Specifically, microscopic visual characterization combined with spectroscopic measurements can help to reveal the structure and the coordination environments of the sample, along with the *in situ* observation of intermediary transformations to profoundly reveal the reaction mechanisms. In addition, theoretical calculations simulating the role of MAS in photocatalysis reveal the physical and chemical properties exhibited by MAS during CO₂ conversion.¹³⁵

4.1 High-resolution aberration-corrected high-angle annular dark-field scanning transmission electron microscopy (AC-HAADF-STEM)

In the structural characterization of single-atom catalysts, high-resolution AC-HAADF-STEM demonstrates paramount importance in elucidating the distribution of the MAS and its geometry. Isolated Co single-atom-modified 2D monolayer ZIS nanosheet composites (Co-^sZIS) possessed dual active centers of Co and Zn.¹³⁶ AC-HAADF-STEM was used to characterize the dispersion and configuration of the atoms involved, and to assist in determining the atomic structure of Co-^sZIS. Fig. 11a clearly shows the distribution of isolated Co atoms in ^sZIS, with the yellow circles marking the atomic spots that were brighter compared to the surrounding support. Fig. 11b and c reflects the fact that the corresponding atoms exhibited different

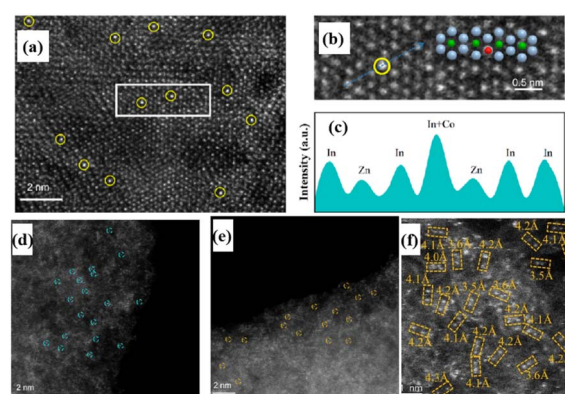


Fig. 11 (a) Aberration-corrected HAADF STEM image of the Co-^sZIS; single-atomic Co sites are highlighted by yellow circles. (b) Magnified view of the white box in (a) (inset is the simulated atom distribution of Co-^sZIS, and the green, gray, and red spheres represent the Zn, In, and Co atoms, respectively). (c) Intensity profile corresponding to the dark cyan arrow in (b). These figures have been reproduced from ref. 136 with permission from American Chemical Society, copyright 2023. Aberration-corrected HAADF-STEM images of (d) Ni–N–C, (e) Fe–N–C, and (f) (Ni, Fe)–N–C. These figures have been reproduced from ref. 137 with permission from Wiley–VCH, copyright 2023.



contrasts, with one of the largest peaks corresponding to the overlapping intensity spectra of an In atom and the individual Co atom. In addition, AC-HAADF-STEM was used to further examine the detailed distribution state of the MAS. The bright spots in Fig. 11d and e confirmed the isolated dispersion of Ni or Fe atoms on the carbon skeleton of the Ni-N-C and Fe-N-C single-atom catalysts, respectively, and no atom pairs were observed. In contrast, the AC-HAADF-STEM images of the (Ni, Fe) dual-single-atom catalysts (Fig. 11f) clearly showed most of the bright spots appearing in pairs, marked by yellow rectangles, confirming the formation of Ni/Fe dual-atom pairs with an average distance of about 4.1 Å.¹³⁷

4.2 X-ray photoelectron spectroscopy (XPS)

XPS is considered to be an effective method to analyze the surface properties of the catalysts, reflecting the chemical bonding composition and the migration paths of carriers based on peak shifts. Porous covalent triazine frameworks (CTFs) were combined with CdS nanorods to obtain CdS@CTF-HUST-1 heterojunction photocatalysts with core-shell structures for CO₂-to-CO conversion.¹³⁸ Essentially, the full XPS spectra showed the coexistence of Cd, S, C and N elements in the CdS@CTF-HUST-1 with an optimal CdS content, referred to as Cd(0.9)@CTF. *In situ* XPS was conducive to revealing S-scheme charge transfer mechanisms of CdS@CTF-HUST-1. As shown in Fig. 12, the Cd 3d and S 2p peaks of the CdS(0.9)@CTF sample showed a positive displacement with respect to CdS, while the C 1s and N 1s peaks of CdS(0.9)@CTF exhibited a negative shift relative to CTF-HUST-1 under dark conditions. Such shifts indicated the interfacial transfer pathway of electrons from CdS to CTF-HUST-1. Under light illumination, the binding energies of Cd 3d and S 2p of the CdS(0.9)@CTF were negatively shifted compared to those in darkness, while the binding energies of C 1s and N 1s underwent positive

displacement. These peak shifts confirmed that the internal electric field could drive the transfer of photogenerated electrons from CTF-HUST-1 to CdS under light irradiation. Furthermore, *in situ* irradiated XPS validated the Z-scheme charge transfer path of Ni-doped CsPbBr₃/Bi₃O₄Br with an internal electric field directing from Ni-doped CsPbBr₃ to Bi₃O₄Br.¹¹⁴ The binding energies of Cs, Pb and Br of CsPbBr₃ were all positively shifted upon Ni doping, suggesting that the introduced Ni sites interacted with the surrounding atoms to reduce the electron density around the Cs, Pb and Br atoms. After composing the heterostructure, the Cs 3d and Pb 4f of Ni-doped CsPbBr₃/Bi₃O₄Br were shifted to higher binding energy by 0.3 eV with respect to Ni-doped CsPbBr₃, whereas Bi 4f and O 1s underwent a 0.2 eV shift to lower binding energy with respect to Bi₃O₄Br. In addition, the distance between the Br 3d_{5/2} and Br 3d_{3/2} peaks increased, indicating an enhanced spin-orbit splitting function of Br 3d. These results revealed changes in the charge loss and accumulation states of Ni-doped CsPbBr₃ and Bi₃O₄Br in the heterostructures, demonstrating the strong interfacial interaction between Bi₃O₄Br and Ni-doped CsPbBr₃. Upon illumination, Cs 3d and Pb 4f moved toward lower binding energies relative to the characteristic peaks in the dark environment, while Bi 4f and O 1s exhibited significant positive shifts. These results suggested that the light-induced electrons follow a Z-scheme path from Bi₃O₄Br to Ni-doped CsPbBr₃.

4.3 X-ray absorption fine structure (XAFS)

Based on synchrotron radiation, XAFS has become an important technique to reveal the electronic structure, coordination number and bonding environment of MAS, and is widely used to study MAS-containing catalytic systems. Specifically, the technique is usually classified into X-ray absorption near-edge structure (XANES) and extended X-ray absorption fine structure (EXAFS).¹³⁹

Cu-N₄ sites-anchored phosphorus-modulated carbon nitride (CuACs/PCN) regulated the intermediate energy levels to achieve C₂H₄ formation during CO₂ photoreduction.⁸⁵ The Cu K-edge XANES of CuACs/PCN was between Cu₂O and CuO (Fig. 13a), indicating that the oxidation state of Cu is between +1 and +2. In the EXAFS spectrum (Fig. 13b), CuACs/PCN had a prominent peak near 1.5 Å, corresponding to the scattering of the Cu-N bond in the first coordination shell. The absence of the Cu-Cu coordination (2.2 Å) indicated that the Cu sites were atomically dispersed. From the fitting results (Fig. 13c), Cu atoms in CuACs/PCN were coordinated by four N atoms at a distance of 1.97 Å. The wavelet transform contour plot of CuACs/PCN exhibited a radial distance of 1.5 Å (Y-axis), which was significantly different from that of the Cu foil. These results strongly demonstrated that Cu atoms were dispersed with Cu-N₄ coordination in CuACs/PCN. In addition, XAFS was applied to study the coordination environment of MAS in Co₁Ag_(1+n)-PCN.¹¹⁰ In the Ag K-edge XANES spectra, the near-edge absorption peak of Co₁Ag_(1+n)PCN was located above Ag₂O, indicating that the valence state of Ag was near +1 (Fig. 13e). Two main peaks at 1.5 and 2.4 Å in the Fourier-transformed Ag k²-weighted EXAFS spectra (Fig. 13f) corresponded to the first

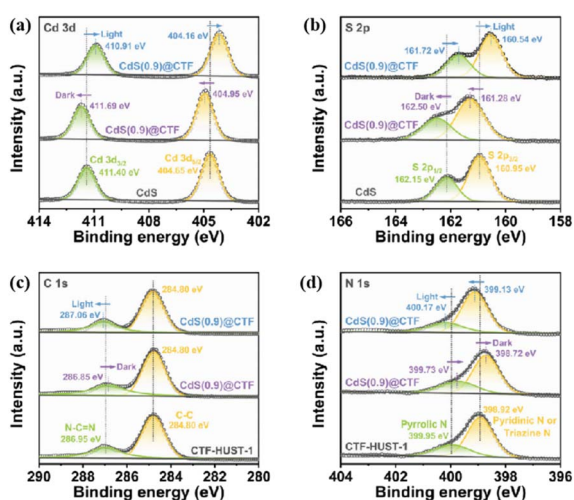


Fig. 12 High-resolution XPS spectra of (a) Cd 3d, (b) S 2p, (c) C 1s, and (d) N 1s of CdS, CTF-HUST-1, and CdS(0.9)@CTF samples. The *in situ* XPS measurement was performed under light irradiation. These figures have been reproduced from ref. 138 with permission from Wiley-VCH, copyright 2023.



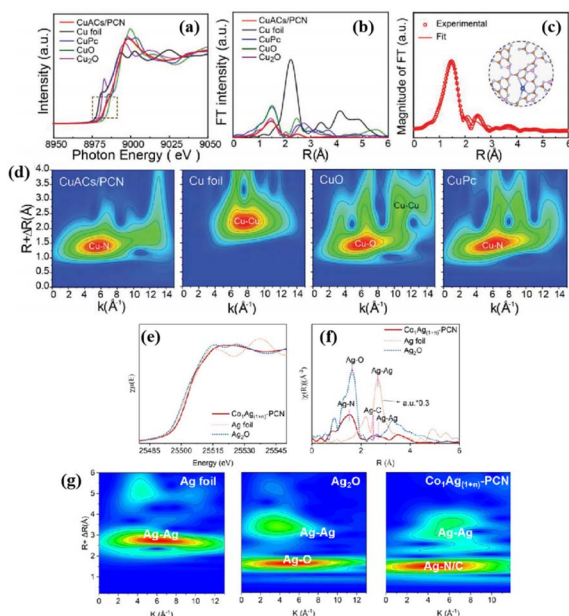


Fig. 13 (a) XANES and (b) EXAFS spectra of the Cu K-edge of CuACs/PCN, Cu foil, Cu_2O , CuO, and CuPc. (c) The EXAFS fitting curves of CuACs/PCN at R -space. (d) WT EXAFS of the Cu K-edge. These figures have been reproduced from ref. 85 with permission from Wiley-VCH, copyright 2022. Ag K-edge (e) XANES, (f) EXAFS, and (g) WT-EXAFS spectra of $\text{Co}_1\text{Ag}_{(1+n)}$ -PCN. These figures have been reproduced from ref. 110 with permission from American Chemical Society, copyright 2023.

shell layer of Ag–N and the second shell layer of Ag–C, respectively. The presence of Ag–Ag coordination (2.6 Å) indicated that Ag existed in the form of single atoms and nanoparticles. The wavelet transform Ag K-edge EXAFS of $\text{Co}_1\text{Ag}_{(1+n)}$ PCN showed a maximum peak around 4.7 Å, which was different from that of the Ag foil and Ag_2O , attributed to Ag–N/C coordination. Specifically, the EXAFS fitting of the shell coordination elucidated that the Ag atom was coordinated to 2.3 N atoms and 1.7C atoms, referred as the Ag– N_2C_2 site. Based on a similar analytical procedure, the existence of a Co– N_6 –P configuration of the Co single atom in $\text{Co}_1\text{Ag}_{(1+n)}$ PCN was also revealed.

4.4 Diffuse reflectance infrared Fourier-transformed spectroscopy (DRIFTS)

DRIFTS can be used to deduce the structure of the compound, reflecting the type of functional groups contained in the substance. Characterization of intermediates generated on the catalyst surface using *in situ* DRIFTS provides support for the reaction pathway revelation and MAS identification. *In situ* DRIFTS was used to probe the reaction intermediates in the CO_2 photoreduction of Er-doped ZnIn_2S_4 .⁸⁶ Under dark conditions, Er-doped ZnIn_2S_4 exhibited distinct absorption peaks corresponding to monodentate carbonate ($m\text{-CO}_3$) and bidentate carbonate ($b\text{-CO}_3$), indicating the effective adsorption and activation of CO_2 and H_2O . Under light conditions, the peaks of $^*\text{CHO}$ (962 cm^{-1}), $^*\text{OCH}_3$ (1043 cm^{-1}) and $^*\text{COOH}$ (1530 cm^{-1}) appeared in Er- ZnIn_2S_4 , which were the key intermediates for the subsequent generation of CH_4 . Both Er- ZnIn_2S_4 and pure

ZnIn_2S_4 showed absorption peaks for the $^*\text{CH}_2$ group at 2856 and 2935 cm^{-1} , respectively, reflecting their tendency to generate CH_4 . Compared to pure ZnIn_2S_4 , the Er- ZnIn_2S_4 exhibited stronger $b\text{-CO}_3$ dissipation with stronger CO_2 reduction capacity. The spectrum of Er- ZnIn_2S_4 had additional $^*\text{OCH}_2$ peaks between $1210\text{--}1240\text{ cm}^{-1}$, reflecting different CO_2 reduction pathways between Er- ZnIn_2S_4 and ZnIn_2S_4 (Er- ZnIn_2S_4 : $\text{CO}_2 \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow ^*\text{CHO} \rightarrow ^*\text{OCH}_2 \rightarrow ^*\text{OCH}_3 \rightarrow \text{CH}_4$; ZnIn_2S_4 : $\text{CO}_2 \rightarrow ^*\text{COOH} \rightarrow ^*\text{CO} \rightarrow ^*\text{CHO} \rightarrow ^*\text{CH}_2\text{O} \rightarrow ^*\text{CH} \rightarrow ^*\text{CH}_2 \rightarrow ^*\text{CH}_3 \rightarrow \text{CH}_4$).

In situ DRIFTS identifies key intermediates of the C_{2+} product, contributing to the inference of C–C coupling processes. In this regard, crucial C_2 intermediates including COCO^* (1374 and 1486 cm^{-1}) and COCO^*H (1233 and 1574 cm^{-1}) were observed on the Au– CeO_2 nanocomposite, providing strong evidence that the Au–O–Ce sites drove the generation of C_2H_6 from the C–C coupling.⁹⁷ In addition, the peaks at 1367 and 1485 cm^{-1} appearing in the $\text{In}_2\text{O}_3/\text{InP}$ heterojunction were related to OCCO^* , a key intermediate in the generation of CH_3COOH .¹²⁰ The peak at 1332 cm^{-1} belonged to the C–H vibration of the hydrogenated intermediate after C–C coupling, and the peak at 1433 cm^{-1} belonged to the COO stretching vibration of CH_3COOH , further reflecting the generation of C_{2+} .

4.5 Raman

Raman spectroscopy identifies chemical bonds and functional groups. *In situ* Raman spectra can reveal the structural evolution of catalysts during catalytic reactions. For Vo-rich Zn_2GeO_4 , CO_2 adsorption on Ge and Zn atoms gradually shifted the peak positions of the Zn–O–Ge stretching vibrations ($\sim 730\text{ cm}^{-1}$) and Zn–O–Ge bending vibrations ($\sim 785\text{ cm}^{-1}$) to higher wave numbers.⁹⁶ The Raman peak blue shift revealed the transfer of the electron cloud from the lattice oxygen to the metal atoms. The Zn–O–Ge stretching and Zn–O–Ge bending vibration peaks were again shifted to higher frequencies during CO_2 photoreduction, indicating that the electron cloud in the O 2p orbitals of the lattice oxygen was further transferred to the nearby Zn 4s or Ge 4s empty orbitals. This process provided electrons for the reduction of adsorbed CO_2 molecules and reaction intermediates. *In situ* Raman enables the real-time monitoring of the intermediate generation and conversion processes on the catalyst surface, revealing the reaction mechanism. In the *in situ* Raman spectrum, the peak before 500 cm^{-1} was related to the structural properties of r- $\text{In}_2\text{O}_3/\text{InP}$.¹²⁰ With increasing light duration, the peak at 887 cm^{-1} was designated as C–C–O stretching, reflecting the critical C–C coupling process for CH_3COOH generation. The $\text{C}\equiv\text{O}$ stretching vibration of CO^* (2909 cm^{-1}) further validated that the CO^* coupling produced CH_3COOH .

4.6 Electrochemical analysis

Electrochemical analysis is widely used to reveal the kinetic processes of the migration and separation of photogenerated carriers in photocatalysis. Among them, transient photocurrent response and electrochemical impedance measurement (EIS)



are the most representative and widely used methods.^{140–144} For example, the Cu–N₄ sites-anchored phosphorus-modulated carbon nitride (CuACs/PCN) exhibited the strongest photocurrent response relative to carbon nitride (CN), CuACs-anchored carbon nitride (CuACs/CN), and CuACs/PCNs with different P doping contents, reflecting its superior interfacial charge separation efficiency.⁸⁵ Moreover, EIS also demonstrated the lowest resistance of CuACs/PCN, thus confirming the efficient separation of photoexcited electron–hole pairs.

As another crucial feature, electrochemical analysis contributes to reveal the change of activation and reduction energy of CO₂ conversion. Kang's research group examined the Tafel plots of pure Cu, Cu/PVP and Cu/rGO/PVP/Nafion composite electrodes to estimate the reaction overpotentials of the samples.¹⁴⁵ The overpotentials of Cu/PVP (6.16 kJ mol^{−1}) and Cu/rGO/PVP/Nafion (9.00 kJ mol^{−1}) electrodes were significantly lower than those of the pure Cu electrode, revealing a decrease in the CO₂ reduction energy.

In addition, the Mott–Schottky measurement can be used to specify the semiconductor type and determine the valence band maximum (VBM) and conduction band minimum (CBM) potentials. For example, according to the results of the Mott–Schottky test, the Zr/Ti bimetallic oxide solid solution integrated with Au nanoparticles (Au/TZO) exhibited the characteristics of n-type semiconductors.¹³¹ As the CBM of Au/TZO was estimated as −0.80 V with respect to a normal hydrogen electrode (NHE), the photocatalytic conversion of CO₂ to CO (−0.53 vs. NHE), CH₄ (−0.24 vs. NHE), C₂H₄ (−0.34 vs. NHE) and C₂H₆ (−0.27 vs. NHE) was thermodynamically feasible over Au/TZO. It is also worth mentioning that the electrochemical active surface area (ECSA) can be used to reveal the number of catalytically active sites. A larger ECSA indicates more active sites, which is more favorable for photocatalytic CO₂ conversion.¹⁴⁶

4.7 Theoretical calculations

Theoretical calculations can be used to obtain the atomic and electronic structures of the MAS, the adsorption strength of the intermediates, and the optimal reaction path.

Electronic property analysis can infer underlying factors affecting the catalytic activity. The d-band centers of Cu in Cu₁N₃@P(1)CN, Cu₁N₃@CN, and Cu₁P₃@PCN were determined to be −1.24 eV, −1.46 eV, and 11.60 eV, respectively, by partial density of states analysis, which depended on the local coordination environment of Cu.⁸⁷ As the d-band center of Cu approached the Fermi energy level, the catalytic activity for the COOH* formation became higher. It is worth mentioning that the overlap between Cu 3d and P 3p in Cu₁N₃@P(1)CN was more pronounced than the overlap of Cu 3d with C 2p at the same corner position in Cu₁N₃@CN. This reflected the more pronounced orbital and electronic interactions of Cu and P in Cu₁N₃@P(1)CN than that of Cu and C in Cu₁N₃@CN, which moved the d-band center of Cu₁N₃@PCN closer to the Fermi energy level. Charge density difference analysis further demonstrated that the electronic interaction between Cu and COOH* in Cu₁N₃@P(1)CN was the strongest relative to Cu₁N₃@CN and Cu₁P₃@PCN, prompting a large number of

electrons to be transferred from the Cu center to COOH* in Cu₁N₃@P(1)CN, benefiting CO₂ activation.

Theoretical calculations provide insight into the mechanism of the photocatalytic CO₂ reduction reaction. From the free energy analysis, the introduction of Ag single atoms on hollow porous polygonal C₃N₄ nanotubes (Ag₁@PCNT) significantly enhanced the adsorption of *CO₂ and weakened the adsorption of *H, suggesting that Ag₁@PCNT was more favorable for CO₂ conversion than for hydrogen production.⁸⁸ The COOH* formation energy (the rate-limiting step) of Ag₁@PCNT was lower than that of C₃N₄ nanotubes. This suggests that the strong interaction of the Ag–N₃ coordination with *COOH stabilized the *COOH intermediate and reduced the barrier for CO₂ photoreduction (Fig. 14a and b). In addition, the generation of CO molecules by desorption of *CO groups on the surface of Ag₁@PCNT had a smaller Gibbs free energy than the protonation of *CO into *CHO, which contributed to the highly selective generation of CO.

Theoretical calculations can reveal the specific processes involved in the generation of C₂₊ products, especially for C–C coupling. Calculation of the Gibbs free energy diagrams for CO₂ photoreduction on In and/or Cu-anchored poly-CN (InCu/poly-CN, Cu/poly-CN, and In/poly-CN) (Fig. 14c) revealed that the formation of *COOH was a rate-determining step on InCu/poly-CN ($\Delta G = +1.20$ eV) and In/poly-CN ($\Delta G = +1.86$ eV), while the generation of *COCH₂OH was a rate-determining step on Cu/poly-CN ($\Delta G = +1.98$ eV).⁹⁸ On InCu/poly-CN, *CO underwent a dimerization reaction ($\Delta G = 0.45$ eV) and a subsequent hydrogenation–electron addition process to ultimately generate CH₃CH₂OH. In the Cu/poly-CN system, *CO was also coupled to form *COCO, but its Gibbs free energy was higher than that of the InCu/poly-CN. Furthermore, the process from *COCHOH to *COCH₂OH in Cu/poly-CN was endothermic with the highest gain ($\Delta G = +1.98$ eV), resulting in lower CH₃CH₂OH yields for Cu/poly-CN relative to InCu/poly-CN. However, the *CO

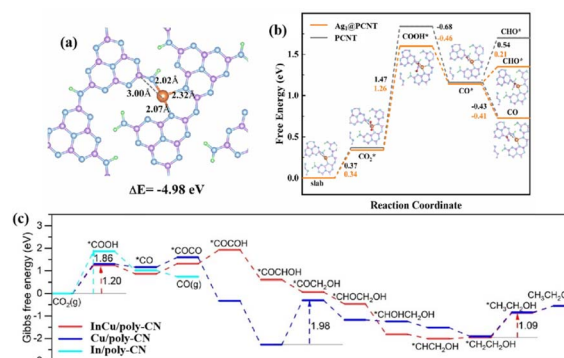


Fig. 14 (a) Structure of Ag₁@PCNT. (b) Gibbs free energies of the CO₂ photoreduction pathways by DFT calculations over the Ag₁@PCNT (Ag sites) and PCNT surfaces. Atom key: N (blue), C (purple), H (green), and Ag (orange). These figures have been reproduced from ref. 88 with permission from Wiley-VCH, copyright 2023. Gibbs free energy diagrams and CO₂-to-ethanol photoreduction pathways on InCu/poly-CN, Cu/poly-CN, and In/poly-CN (c). This figure has been reproduced from ref. 98 with permission from Wiley-VCH, copyright 2022.



intermediates on In/poly-CN preferred desorption as CO products (exothermic) rather than C–C coupling, resulting in a poor $\text{CH}_3\text{CH}_2\text{OH}$ yield on In/poly-CN.

5 Conclusion and perspectives

The photocatalysts containing MAS have been proved as efficient systems for converting incident solar energy into chemical fuel. In this review, typical photocatalytic materials containing MAS have been briefly introduced with clear examples. Then, the different roles of MAS in various forms in the photocatalytic CO_2 reduction from the perspective of principles and applications are discussed in detail, greatly accelerating the surface charge separation/transfer, and enhancing the adsorption and activation of CO_2 . Finally, advanced characterization techniques and theoretical calculation for revealing the function played by MAS in CO_2 photoreduction are presented. Although considerable progress has been made in MAS-containing photocatalytic systems, there are still great challenges in practical applications that need to be further explored.

(1) The complexity of the preparation process and the difficulty of achieving uniform high-volume production are the major drawbacks of MAS-containing catalysts. In addition, the exposed MAS are susceptible to oxidation, resulting in performance degradation. Therefore, effective technologies should be continuously developed for the large-scale production of MAS-containing photocatalysts with stable and controllable surface states. Elaborate design strategies to improve the catalyst stability (*e.g.*, surface encapsulation and ligand grafting) need to be further explored. Continuous optimization of existing synthesis methods is an effective and viable solution.

(2) Although photocatalysts containing MAS have shown great potential in artificial photosynthesis, their performance is still unsatisfactory for practical production. Particularly, photocatalytic CO_2 conversion involves a variety of intermediates and products, making it difficult to regulate the selectivity of the target product. For photocatalytic systems with MAS, the interactions of reactants and intermediates with the MAS affect the activation and conversion of CO_2 , as well as C–C coupling. Defect design, doping, construction of heterostructures, and introduction of co-catalysts have become widely used strategies to enhance the CO_2 photoreduction performance. However, there is still a need to continuously explore effective and novel strategies to improve the performance for real-world production, which remains elusive at the present stage.

(3) Accurate characterization and in-depth understanding of the mechanism of MAS in photocatalysis still face great challenges. It is crucial to carefully reveal the coordination environments of the MAS and its changes during the photocatalytic reaction. Specifically, the working mechanism of MAS in photocatalysis can be explored in-depth by advanced *in situ* characterisation techniques and accurate theoretical calculations, which guide the rational design and regulation of photocatalysts. Therefore, there is a need for the continuous development of highly sophisticated characterisation techniques, and theoretical computational models close to the actual reaction processes.

(4) In the face of the explosion of research data, the traditional research method of relying on pre-investigation to identify scientific problems has become overwhelming. This approach is costly, time-consuming, and increasingly difficult to meet the research needs of modern materials science. Nowadays, machine learning is changing the traditional research paradigm and bringing new opportunities for the development of related technologies and industrial upgrading. Combining machine learning techniques with the design of photocatalytic systems to rapidly mine effective information from a large amount of data is conducive to the construction of novel materials and the excavation of reaction mechanisms. Specifically, machine learning techniques are becoming a powerful tool for scientific research in the design and construction of photocatalysts, as well as in the prediction of physicochemical properties and mechanisms.

In summary, through continuous exploration and in-depth research, it is found that photocatalytic CO_2 reduction technology is expected to realize the establishment of a resource-saving and environmentally-friendly energy system, and improve human life in the near future.

Data availability

No primary research results, software or code have been included and no new data were generated or analysed as part of this review.

Author contributions

All authors participated in this review work. W. Gao, Y. Yang, and Y. Zhou conceived the structure of this perspective. W. Gao, H. N. Li, and J. Q. Hu prepared the draft. Y. J. Xiong, J. H. Ye, and Z. G. Zou reviewed and refined the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

The authors wish to acknowledge the support of the National Key R&D Program of China (2018YFE0208500 and 2021YFA1500700), the NSF of China (21972065 and 22202152), the NSF of Jiangsu Province (No. BK20220006), the Hefei National Laboratory for Physical Sciences at the Microscale (KF2020006), the Program for Guangdong Introducing Innovative and Entrepreneurial Team (2019ZL08L101) and the University Development Fund (UDF01001159).

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