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REVIEW

Recent advances in novel materials for photocatalytic carbon dioxide reduction

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Abstract

The conversion of CO₂ into chemical fuels, which can be stored and utilized through photocatalysis, represents an effective, environmentally friendly, and sustainable means to address both environmental concerns and energy shortages. CO₂, as a stable oxidation product, poses challenges for reduction through light energy alone, necessitating the use of catalysts. Thus, a crucial aspect of CO₂ photocatalytic reduction technology lies in the development of effective photocatalysts. Based on the basic principle of PCRR (photocatalytic CO_2 reduction reaction), the review provides a detailed introduction to the core issues in PCRR process, including the relationship between band gap and catalyst reduction performance, effective utilization of photogenerated carriers, product selectivity, and methods for product analysis. Then, the recent research progresses of various photocatalysts are reviewed in the form of research examples combined with the above basic principles. Finally, this review summarizes and provides insights into the effective techniques for enhancing the photocatalytic activity of CO₂, while also offering future prospects in this field.

KEYWORDS

carrier-hole, CCUS, CO2 reduction, photocatalysis, photocatalyst

Shanyue Lu, Shengwei Zhang, and Qi Liu contributed equally to this study.

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1 | INTRODUCTION

As the world population continues to grow at a rapid pace and modern economies experience swift development, the global demand for energy has been on a constant rise.^[1] The average atmospheric CO_2 concentration has increased dramatically over the last several years to above 410 ppm, which represents a staggering 45% increase compared with levels observed during the Industrial Revolution. This increase is largely attributable to the excessive utilization of fossil fuels.^[2,3] The safety and well-being of individuals and other organisms are seriously threatened by the significant CO₂ emissions causing the greenhouse effect, as they contribute to the alarming rise in global temperatures. Numerous efforts have been undertaken to tackle these challenges, including the capture, storage, and utilization of CO_2 (CCUS).^[4–6] Three approaches exist for controlling the level of CO_2 in the atmosphere: (1) Reduction of CO₂ emissions, (2) Capture and storage, and (3) Converting CO_2 into high-value-added chemical products. Among these approaches, the transformation of CO₂ into high-value chemicals through catalytic reactions, thus decreasing the amount of CO₂, shows great promise. CO₂ molecules are highly stable from a thermodynamic standpoint, with C=O bond energies reaching as high as 750 kJ mol^{-1} . Furthermore, CO₂ reduction tends to involve a single electron transfer step rather than a concerted multielectron transfer process, resulting in a sluggish kinetic process.^[7] As a result, the decomposition of CO₂ is an arduous and energy-intensive task when conventional methods are employed. Currently, numerous methods such as biocatalysis,^[8,9] thermocatalysis,^[10–12] photocatalysis,^[13–15] and electrocatalysis^[16–18] have been investigated with promising outcomes for CO₂ reduction. The process of biocatalysis involves the use of enzymes that are less stable and prone to deactivation. Meanwhile, thermocatalytic CO₂ reduction typically necessitates higher reaction temperature and pressure, and more significant Gibbs free energy to propel the reaction, which may have adverse implications for the process's sustainability and economic feasibility.^[19] Among all the various renewable energy solutions, solar energy is seen to be one of the most promising, owing to its abundance, direct availability, cost-effectiveness, and cleanliness. The process of photocatalytic CO₂ reduction, which mimics the natural photosynthesis observed in plants, has attracted significant attention for its environmentally friendly, clean, and pollution-free characteristics. Utilizing solar energy to convert CO₂ into chemical fuels or other valuable chemicals has further contributed to its prominence.^[20]

The catalytic effectiveness of photocatalysts is significantly impacted by several factors, including the scarcity

of active catalytic sites, facile charge recombination, instability, and limited utilization of visible light. Despite the tremendous challenge posed by CO₂ conversion, it is possible to convert CO₂ into high-value compounds by creating the right photocatalysts, which can overcome kinetic and thermodynamic barriers and advance the reaction. Currently, multiples of photocatalytic materials such as metal oxides, carbon materials, metal-organic frameworks, metal sulfides, MXenes, perovskites, plasmonic materials, quantum dots (QDs), single-atom materials are frequently employed for photocatalytic CO_2 reduction.^[21-33] To explore and build more sensible photocatalytic materials that reduce CO₂ more effectively, a comprehensive and up-to-date overview of the latest research advancements in this area is essential. This review aims to emphasize the fundamental mechanisms of photocatalytic CO₂ reduction, and present a summary of the most recent advances in this field using different materials. Lastly, based on our present comprehension, we suggest potential future research directions. We expect that researchers working on the design and development of photocatalytic materials will find this review to be a useful resource.

2 | FUNDAMENTAL PRINCIPLES RELATED TO PCRR

As shown in Figure 1, PCRR proceeds through the following five steps: (1) Generation of electron-hole pairs. Under irradiation by light with sufficient energy (where photon energy is larger than or equal to the band gap energy), the photocatalyst causes electrons to transition from the valence band (VB) to the conduction band (CB), leading to the generation of numerous electron-hole pairs. The carriers in the CB serve as reducing agents, while the holes in the VB serve as oxidizing agents; (2)



FIGURE 1 Elementary steps occurring in a photocatalytic reduction of CO₂. Reproduced with permission: Copyright 2017, John Wiley and Sons.^[34]

Separation of carriers from the bulk material and their transfer to the surface of the photocatalyst. During this process, the carriers are highly susceptible to recombining with holes, resulting in a decrease in the number of free electrons in the CB and its corresponding reduction capacity, ultimately impacting the overall photocatalytic efficiency. Thus, it is crucial to suppress carrier recombination and enhance their generation rate to improve the efficiency of photocatalysis; (3) The capture and activation of reactants (CO₂ and H₂O) occur concurrently on the surface of the photocatalyst; (4) The electrons efficiently migrate to the active surface sites and catalyze the reduction of CO_2 ; (5) The resulting products are desorbed from the surface of the photocatalyst, and the exposed surface active sites continue to take part in the catalytic reaction. However, the reduction products may occupy these active sites, impeding subsequent responses. Hence, the desorption of the products is crucial in the total photocatalytic process.^[35] In the following sections, we will provide a detailed description of several critical issues in the CO₂RR process.

2.1 | The constraint relationship between light absorption and reduction properties of catalysts

Similar to most photocatalytic reactions, the photoabsorption capacity of the catalyst is an important influence on the conversion efficiency of CO₂. The energy band structure of a photocatalyst plays a critical role in determining its light absorption ability. The light absorption properties of typical materials can be categorized into ultraviolet (<400 nm), visible (~400-760 nm), and near-infrared (>760 nm) regions. Within the solar spectrum, visible and near-infrared light make up 95%, while ultraviolet light constitutes only 5%.^[36] Materials that have the ability to absorb visible and near-infrared light can more efficiently harness solar energy for catalytic reactions. Nevertheless, many commonly used semiconductor materials have band gaps that limit their ability to absorb light across broader wavelength ranges, leading to lower overall solar energy utilization. In the PCRR process, the CB edge of the photocatalyst is typically smaller than the reduction potential of CO_2 , while the VB edge is larger than the oxidation potential of the oxygen precipitation reaction (OER), as shown in Figure 1.^[34,37] To mitigate the high overpotential required for both reactions, the material's band gap needs to be sufficiently wide. While the energy bands of wide-bandgap (>3 eV) semiconductor materials are suitable for mediating redox processes, they tend to only

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respond to the UV region. For instance, TiO₂, exhibits limited light absorption because of its wide band gap (>3 eV), resulting in a poor CO₂ conversion rate. However, materials with narrow band gaps (<3 eV) are more sensitive to visible-near-infrared light, allowing for higher light absorption capacity and efficient CO₂ reduction. A narrow bandgap, on the other hand, results in a higher rate of electron-hole complexation compared with the electron production rate, which hinders the improvement of photocatalytic quantum efficiency.^[1] Moreover, the reduction and oxidation potentials of narrow bandgap materials are not sufficiently high, which can impede the CO₂RR and OER reaction on the catalyst surface. Therefore, developing CO₂photosensitive materials with appropriate energy band structures is one of the priorities in photocatalysis.

2.2 | Effective utilization of photogenerated carriers

Because CO₂RR reaction is driven by photogenerated carriers on the catalyst surface, the generation and transport efficiency of charge carriers directly affect the catalytic efficiency. The density of carriers present on the surface of the photocatalyst is contingent upon both effectiveness of electron-hole separation as well as the proficiency of carrier migration from the bulk to the photocatalyst surface, as shown in Figure 3a.^[36] The primary hindrances to this process include the complexation of electrons and holes between the bulk phase and the surface, as well as the substantial differences in rates of electron transfer and electron-hole complexation.^[1] Throughout the migration process, carriers are highly prone to be complex with holes as a result of Coulomb attraction, leading to a significant decrease in free electrons on the CB, thereby lowering the electron density. The absorbed energy of these electrons is released as heat, consequently impeding their involvement in redox reactions occurring on the surface.^[38] Typically, there exists a close correlation between carrier mobility and the intrinsic-to-surface distance, while the surface complexation may stem from the catalyst surface not having a sufficiently large number of active sites or capture states, and can also be attributed to the intricate interplay between microcrystalline structure, size, surface properties, and other structural factors present in the catalyst. The production of photocatalysts with elevated intrinsic mobility and efficient charge separation is paramount for successful PCRR. This can be achieved through optimization of the material structure, such as metal doping and adjusting the crystal surface, it decreases the possibility of carrier compounding and improves the separation

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effectiveness of photogenerated carriers. Furthermore, electron transfer at semiconductor interfaces is hundreds or thousands of times slower than electron-hole complexation rates. To counteract this issue, hole-trapping agents such as triethanolamine, ethanolamine, or isopropyl alcohol may be employed to consume holes, thereby helping to inhibit electron-hole complexation.^[38–41] In addition, solvents such as acetonitrile, ethyl acetate, or aqueous carbonic acid can be added to the reaction system, and these solvents can dissociate on the surface of the catalyst to produce more H⁺ to participate in the PCRR. Some solvents display photoactive traits, potentially undergoing decomposition and yielding CO₂ reduction products under specific conditions.^[42] Consequently, it becomes crucial to discerningly selecting suitable hole traps or organic solvents, aligning with the distinct attributes of photocatalysts and reaction settings. This meticulous selection serves to mitigate the risk of overestimating both CO₂ reduction yield and product selectivity.^[43] It is worth mentioning that the choice of solvent in the reaction system can affect the activity and selectivity of the photocatalyst. Certain solvents can induce more favorable interactions between the catalyst and the substrate, thus improving product selectivity.^[44] On the other hand, the polarity and solubility of the solvent may also affect the activity of the catalyst.^[44]

2.3 | Mechanism and selectivity

 CO_2 reduction involves various steps such as activation, adsorption, and surface reactions, all of which are dependent on the number of electrons generated, electron and proton transfer, hydrogenation and deoxygenation processes, C-O bond breaking, C-H bond generation, and so forth.^[45] As shown in Figure 2, the pathways of CO_2 reduction include formaldehyde, carbene, and glyoxal pathways, which start with the adsorption of CO_2 molecules on the surface of catalysts and activation.^[1,46] The adsorption of CO_2 on the surface of catalysts is crucial for successful CO_2 reduction, and there are three main modes of CO_2 adsorption: carbon coordination, oxygen coordination, and mixed coordination (Figure 3).^[47]

In the formaldehyde pathway, the O within CO_2 undergoes binding to the active site of the catalyst, initiating CO_2 activation. Electron transfer to CO_2 leads to the generation of a CO_2 radical (CO_2^{-}). This radical subsequently engages with a proton, resulting in the formation of -COOH. The ensuing reaction involves the interaction of -COOH with both an electron and a proton, yielding HCOOH. Within this pathway, CO_2 exhibits multiple selectivity in its conversion, giving rise to HCHO, CH_3OH , and CH_4 . The generation of specific



FIGURE 2 General pathways for photocatalytic CO₂ reduction. Reproduced with permission: Copyright 2022, Royal Society of Chemistry.^[1]

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FIGURE 3 (a) Schematic of charge separation and transfer in a photocatalyst. Reproduced with permission: Copyright 2019, John Wiley and Sons.^[36] (b) Three different modes of CO₂ adsorption. Reproduced with permission: Copyright 2023, Elsevier.^[47]

TABLE 1 CO₂ reduction reaction equation and the corresponding standard redox potential versus NHE.

Reaction	E ^o (V vs. NHE)	Eqn
$\rm CO_2 + e^- \rightarrow \rm CO_2^{}$	-1.90	(1)
$\mathrm{CO}_2 + 2\mathrm{H}^+ + 2\mathrm{e}^- \rightarrow \mathrm{CO} + \mathrm{H_2O}$	-0.53	(2)
$\rm CO_2$ + 2H ⁺ + 2e ⁻ \rightarrow HCOOH	-0.61	(3)
$\rm CO_2 + 4H^+ + 4e^- \rightarrow \rm HCHO + \rm H_2O$	-0.48	(4)
$\mathrm{CO}_2 + 6\mathrm{H}^{\!+} + 6\mathrm{e}^{\!-} \rightarrow \mathrm{CH}_3\mathrm{OH} + \mathrm{H}_2\mathrm{O}$	-0.38	(5)
$\mathrm{CO}_2 + 8\mathrm{H}^{+} + 8\mathrm{e}^{-} \rightarrow \mathrm{CH}_4 + 2\mathrm{H}_2\mathrm{O}$	-0.24	(6)
$\mathrm{CO}_2 + 8\mathrm{H}^{\!+} + 8\mathrm{e}^{\!-} \rightarrow \mathrm{CH}_3\mathrm{COOH} + 2\mathrm{H}_2\mathrm{O}$	-0.31	(7)
$\mathrm{CO}_2 + 14\mathrm{H}^+ + 14\mathrm{e}^- \rightarrow \mathrm{C}_2\mathrm{H}_6 + 4\mathrm{H}_2\mathrm{O}$	-0.51	(8)

products depends on the number of electrons and protons available. Among them, $-CH_3$ is a critical intermediate in the formation of CH_4 , and its stability is essential for the formation of CH_4 .^[45]

In the carbene pathway, CO_2 can form a *CO intermediate by combining with two pairs of electrons and protons, at which point *CO can either be desorbed to become a CO product or used as an intermediate to obtain -CH₃ by further hydrogenation, which then reacts with -OH or protons to receive CH₃OH and CH₄, respectively. Currently, the carbene pathway is shown to be the most critical mechanism for the production of CO and other hydrocarbons by the most common mechanism. The reaction steps for some of the products are shown in Table 1.

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Another conversion pathway is the glyoxal pathway, where $CO_2^{\bullet-}$ reacts with electrons and protons to generate formate, which then couples with H⁺ to produce HCOOH. Subsequently, the reaction continues to generate glyoxal. In this pathway, the formation of CH_4 also occurs due to the combination of $-CH_3$ with protons. $-CH_3$ can also form C_2 products, depending on the existence of other intermediates and the ability to couple with them.^[48]

Despite the significant progress made in various studies on reducing CO_2 to C_1 products such as CO, HCOOH, and CH₄, there are still significant challenges in converting C_2 products, which is because PCRR is a complex reaction involving multiple reaction steps, intermediates, and by-products.^[7] In addition, the rapid hydrogenation of intermediates to form C_1 products and the repulsive forces between the oppositely charged intermediates hinder the C-C coupling, resulting in the more difficult generation of C_2 products.^[49]

The selectivity of the products is influenced by several factors, and different reaction pathways may yield alternative reduction products (some of the reaction steps are shown in Table 1). The product selectivity is thermodynamically affected by the nature and structure of the photocatalyst. The reduction process involving multiple electrons is kinetically influenced by the number of electrons and holes generated by photoexcitation, which ultimately affects the product selectivity. In addition, the surface catalytic active site and the adsorption and desorption of reactants and intermediates are all critical kinetic factors that can influence product selectivity.^[35] It is worth noting that H_2O , as a proton source, plays a critical role in CO₂ reduction, and the competing hydrogen evolution reaction (HER) occurring in H_2O can hinder the progress of CO_2 reduction.^[50] Therefore, inhibition of HER should be considered to prevent unwanted by-products from consuming electrons and reducing the yield of the target product.

2.4 | Product measurement

The products of PCRR are diverse and complex, often accompanied by competing HER and OER reactions. The main gas-phase products include CO, O_2 , H_2 , CH_4 , and other hydrocarbons, while the liquid-phase products consist mainly alcohols, aldehydes, and carboxylic acids. The most commonly used method for quantitative analysis and determination of the products is chromatography, including gas and liquid phase chromatography. Gas-phase products such as H_2 , O_2 , and CO_2 and high concentrations of CO, CH_4 , alkanes, and olefins can be quantitatively analyzed by thermal conductivity WILEY- Carbon Neutralization

detector (TCD) in gas chromatography (GC), while low concentrations of CO, CH₄, alkanes, and olefins can be detected by hydrogen flame ionization detector (FID) in GC. For liquid-phase products, alcohols can be quantified using capillary column with FID. Aldehydes can be quantified by high-performance liquid chromatography (HPLC) and UV-vis spectrophotometer (Nash's colorimetric method). Carboxylic acids can be detected by HPLC, ion chromatography (IC), and nuclear magnetic resonance hydrogen spectrometry (¹HNMR). Additionally, mass spectrometry and gas chromatography-mass spectrometry can be utilized for quantitative analysis of gas products and exploration of carbon sources.^[51,52]

An effective catalyst should possess the following characteristics: (1) excellent light absorption ability to generate electron-hole pairs; (2) sufficient active sites on its surface for CO_2 adsorption; (3) the ability to effectively generate and promote the transformation of carriers to the catalyst surface; (4) good stability; (5) a simple and rational synthesis process; (6) high product selectivity; (7) low electron-hole complexation rate; and (8) an appropriate band gap. The above factors should be considered when designing photocatalytic materials to improve the performance of PCRR for various catalytic materials and different reaction conditions.

3 | PHOTOCATALYTIC MATERIALS USED FOR CO₂ REDUCTION

From the principles section mentioned above, it is clear that several elements must be taken into account while choosing and creating photocatalysts, such as light absorption capacity, electron transport properties, active catalytic site, and stability. Nanomaterials have better performance in the above aspects: (1) providing a large specific surface area to facilitate light absorption and full contact with reaction substrates; (2) possessing a large number of catalytic active sites, which is conductive to promoting catalytic reactions; (3) nanostructures can reduce the distance of the electron diffusion (enhance the charge mobility), thereby generating more electronhole pairs (reducing the probability of electron-hole recombination); (4) some of these nanomaterials also have excellent chemical stability.^[53-59] In the following section, the common photocatalysts used for CO₂ reduction are introduced individually according to material classes (including nanomaterial photocatalysts). The properties of different materials are shown in Table 2.

3.1 | Metal oxides

3.1.1 | TiO₂

Since Fujishima et al.^[44] discovered that TiO_2 could produce H_2 under light, researchers have conducted extensive studies on metal oxide catalysts. Among many oxides, TiO_2 is widely used in photocatalysis because of its potential benefits like nontoxicity, good stability, and high photoactivity. Nevertheless, the broadband gap of TiO_2 limits its light utilization and results in poor performance for CO_2 reduction as it can only absorb UV light. The carrier-hole complexation quickly occurs in unmodified or doped TiO_2 .

Metal deposition is an effective means to reduce the carrier-hole complexation rate. Liu et al.^[60] loaded Cu onto different $\tilde{\text{TiO}}_2$ substrates (TiO₂ and H-TiO₂) by ALD, and the experimental findings showed that the CO_2 conversion rate of pristine H-TiO₂ was higher than that of TiO₂, but after depositing Cu by ALD, the photocatalytic CO2 reduction performance of TiO2@50Cu exceeded that of H-TiO₂@50Cu, indicating that the subsequent catalytic performance of different substrates with different physical or chemical properties may be changed after deposition by ALD. Modified photocatalysts with different Pd and Bi loadings were prepared by Moradi et al.^[61] The results showed that the co-catalytic properties formed by bimetallic deposition inhibited the carrier complexation and enhanced the PCRR efficiency, the CH_4 yield was 6.2 times higher than that of pure TiO₂ at the optimum loading, and the stability of 1.5Pt@3Bi-T was excellent. Its CO₂ conversion efficiency could maintain 87% of the initial conversion after six cycles.

Exposed crystalline surfaces have a significant impact on the properties of TiO₂, and by regulating and controlling the exposure of TiO₂ crystalline surfaces, properties such as light trapping and charge separation can be enhanced, thus improving their ability to reduce CO_2 . Jiang et al.^[62] introduced a strong magnetic field in the synthesis of TiO₂, which leaded to the directional splitting of electron orbitals in Ti, and eventually, the formation of new TiO₂ containing more favorable CO* intermediates to undergo coupling to pristine TiO_2 (100) crystal planes.^[62] The lattice distortion induced by the strong magnetic field could be seen from the STEM of Figure 4a, and the different color spots all showed correspondence with the Ti atoms in other crystalline planes, which proved that the strong magnetic field could promote the transformation of the (101) plane of TiO_2 into the (100) plane. With the enhancement of the magnetic field, the yield and selectivity of C₂H₅OH kept increasing. In contrast, the yield of CH4 decreased, which indicated that the enhancement of the magnetic field

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TABLE 2 Various of	materials for	photocatalytic	CO ₂ reduction.
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Type Catalyst	Feed	Light source	Yield	Reference
Metal oxide				
TiO ₂	$CO_2 + H_2O$	300 W Xe lamp	CO: ~79 μmol/g CH₄: ~58 μmol/g	[60]
Pt decorated Bi- doped TiO ₂	CO_2 + Isopropanol	125, 250, and 400 W Hg lamp	CH ₄ : 20.6 µmol/g	[61]
TiO ₂ ({100} Facets)	-	UV-enhanced Xe lamp	CH ₃ CH ₂ OH: 6.16 μmol g ⁻¹ h ⁻¹	[62]
TiO ₂ /WO ₃ -Ag HNPs	A humidified CO_2 gas ($CO_2 + H_2O$ mixture)	A solar simulator with a Si reference cell	CO: 1166.72 μ mol g ⁻¹ h ⁻¹	[63]
$Zn_2Ti_3O_8/ZnTiO_3$	$CO_2 + H_2O$	UV Light	CH ₄ : 0.56 μ mol g ⁻¹ CO: 3.68 μ mol g ⁻¹	[64]
TiO ₂ @ZnIn ₂ S ₄ CSHS	In situ generated CO ₂ + H ₂ O (H ₂ SO ₄ + NaHCO ₃)	300 W Xe lamp	CO: $9.28 \ \mu mol \ g^{-1} \ h^{-1}$ CH ₄ : $4.29 \ \mu mol \ g^{-1} \ h^{-1}$ CH ₃ OH: $4.78 \ \mu mol \ g^{-1} \ h^{-1}$	[65]
Pt-ZnO/ZnS	$CO_2 + H_2O$	300 W Xe lamp	CO: 33.26 μ mol g ⁻¹ h ⁻¹	[66]
ZnO/ZnSe	CO_2 + Isopropanol	250 W Hg lamp (371 nm)	CH ₃ OH: 1581.82 µmol/ gcat/h	[67]
Pt-CsPbBr ₃ /Bi ₂ WO ₆	CO ₂ + Ethyl acetate + Isopropyl alcohol	150 W Xe lamp (AM 1.5 filter)	CO: 103.3 μmol g ⁻¹ CH ₄ : 206.1 μmol g ⁻¹	[68]
Bi_2MoO_6/ln_2S_3	CO_2 + ultrapure water	300 W Xe lamp (λ≥420 nm)	CO: 28.54 μ mol g ⁻¹ h ⁻¹	[69]
Bi ₂ WO ₆ Ovs	$CO_2 + H_2O$	UV-vis light	CH_4 : 9.9 μ mol g ⁻¹ h ⁻¹	[70]
CeO _{2-x}	CO ₂	300 W Xe lamp	CO: 8.25 μ mol g ⁻¹ h ⁻¹	[71]
Carbon materials				
CdS/N-doped graphene	In situ generated CO ₂ (H ₂ SO ₄ + NaHCO ₃)	350 W Xe lamp (420 nm cut off filter)	CO: 2.6 μ mol g ⁻¹ h ⁻¹ CH ₄ : 0.3 μ mol g ⁻¹ h ⁻¹	[72]
TiO ₂ /NG HS	In situ generated $CO_2 + H_2O$ ($H_2SO_4 + NaHCO_3$)	300 W Xe lamp	$CO + CH_4 + CH_3OH:$ 18.11 µmol g ⁻¹ h ⁻¹	[73]
CsPbBr ₃ /USGO/α- Fe ₂ O ₃	Acetonitrile + $H_2O + CO_2$	300 W Xe lamp	CO: 73.8 μ mol g ⁻¹ h ⁻¹	[74]
rGO-Ag-Cu ₂ O	$CO_2 + H_2O$	300 W Xe lamp (380 nm external filter)	CH ₄ : 82.6 μ mol g ⁻¹ h ⁻¹	[75]
KBH-C ₃ N ₄	$CO_2 + H_2O$	300 W Xe lamp (UV- vis light)	CH ₄ : 5.93 μ mol g ⁻¹ CO: 3.16 μ mol g ⁻¹	[76]
MOF				
CTU/TiO ₂	H_2O + pure CO_2	300 W Xe lamp ($\lambda > 300 \text{ nm}$)	CO: $31.32 \mu mol g^{-1} h^{-1}$ CH ₄ : 0.148 $\mu mol g^{-1} h^{-1}$	[77]
PCN-250-Fe ₂ Mn	CH ₃ CN + H ₂ O + Tri isopropanolamine + [Ru(bpy) ₃]Cl ₂ ⋅6H ₂ O + CO ₂	300 W Xe lamp (λ > 420 nm)	CO: 21.51 μ mol g ⁻¹ h ⁻¹	[78]

(Continues)

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TABLE 2 (Continued)

Type Catalyst	Feed	Light source	Yield	Reference
Ni(II)-NH ₂ -MIL- 125(Ti)	Acetonitrile + Triethanola- mine + CO ₂	300 W Xe lamp ($\lambda > 350 \text{ nm}$)	CO: ~5 μ mol g ⁻¹ h ⁻¹	[79]
UiO-66(Zr)	$CO_2 + H_2O$	300 W Xe lamp $(\lambda > 420 \text{ nm})$	CO: 1.33 μ mol g ⁻¹ h ⁻¹	[80]
Metal chalcogenides				
SnS_2/SnO_2	$CO_2 + H_2O$	300 W Xe lamp	CO: 48.01 μ mol g ⁻¹ h ⁻¹	[81]
3DOM CdSQD/NC	$CoCl_2$ + Bipyridine + acetoni- trile + H_2O + benzylamine	300 W Xe lamp (420 nm cut-off filter)	CO: 5210 μ mol g ⁻¹ h ⁻¹	[82]
CuCdS	$CO_2 + H_2O$	300 W Xe lamp	CO: 8.5 μ mol g ⁻¹ h ⁻¹ CH ₄ : 0.7 μ mol g ⁻¹ h ⁻¹	[83]
Bi ₂ O _{2.33} -CdS	$CO_2 + H_2O$	300 W Xe lamp	CO: 2.9 µmol/(cm ² h)	[84]
Mxene				
Cs ₂ AgBiBr ₆ /Ti ₃ C ₂ T _x	$CO_2 + H_2O$	Xenon light	CO: 11.1 μmol g ⁻¹ CH ₄ : 1.3 μmol g ⁻¹	[85]
$Cu\text{-}Ti_3C_2T_x/g\text{-}C_3N_4$	$CO_2 + H_2O$	300 W Xe lamp $(\lambda = 420 \text{ nm})$	CO: 23.87 μmol g ⁻¹ CH ₄ : 1.89 μmol g ⁻¹	[86]
$O\text{-}C_3N_4/Bt/Ti_3C_2T_x$	$CO_2 + H_2O$ + Acetic acid	35 W HID lamp	CO: 365 µmole/g-cat/h CH₄: 955 µmole/g-cat/h	[87]
Perovskites				
Ag (PD)-NiO _x (PD)/CTO	$NaHCO_3 + CO_2$	100 W high-pressure mercury lamp	CO: 7.31 μ mol h ⁻¹	[88]
Cu/CsPbBr ₃ -Cs ₄ PbBr ₆	Ethyl acetate + CO_2	300 W Xe lamp	CO: 185.2 μ mol g ⁻¹ CH ₄ : 149.1 μ mol g ⁻¹	[89]
CsPbBr ₃ @GDY	acetonitrile + H_2O	300 W Xe lamp (400 nm filter)	CO: $10.2 \mu mol g^{-1} h^{-1}$	[90]
ZnSe-CsSnCl ₃	Toluene/Isopropanol solution (45:5, v-v) + CO_2	300 W Xe lamp (400 nm cut-off filter)	CO: 53.96 μ mole g ⁻¹ CH ₄ : 2.55 μ mole g ⁻¹	[21]
Cs ₂ AgBiBr ₆ @g-C ₃ N ₄	Ethyl acetate + Methanol + CO_2	Xe lamp	CO: 2.0 μ mol g ⁻¹ h ⁻¹	[<mark>91</mark>]
$Cs_3Bi_2I_9$	$CO_2 + H_2O$	UV lamp (32 W, 305 nm)	CO: 77.6 μmol g ⁻¹ CH ₄ : 14.9 μmol g ⁻¹	[92]
Rb ₃ Bi ₂ I ₉	$CO_2 + H_2O$	UV lamp (32 W, 305 nm)	CO: 18.2 μmole g ⁻¹ CH ₄ : 17 μmole g ⁻¹	[92]
$MA_{3}Bi_{2}I_{9} \\$	$CO_2 + H_2O$	UV lamp (32 W, 305 nm)	CO: 7.2 µmole g ^{−1} CH₄: 9.8 µmole g ^{−1}	[92]
Plasma				
Au/W ₁₈ O ₄₉ /TiO ₂	$CO_2 + H_2O$	300 W Xe lamp (420 nm filter)	CO: 2.57 μ mol g ⁻¹ h ⁻¹ CH ₄ : 35.55 μ mol g ⁻¹ h ⁻¹	[93]
MoO _{3-x} -TiO ₂	$CO_2 + H_2O$	300 W Xe lamp (420- 780 nm cut-off filter)	CO: 6.8 μ mol g ⁻¹ h ⁻¹	[94]
g-C ₃ N ₄ /TiN	$H_2O + MeCN$ + [Co(bpy) ₃]Cl ₂ + TEOA + CO ₂	300 W Xe lamp (300- 780 nm)	CO: 210.46 $\mu mol g^{-1} h^{-1}$	[95]

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Туре	Catalyst	Feed	Light source	Yield	Reference
Quantum d	dots				
CsPbBr ₃ /C	dSe	$CO_2 + H_2O + ethyl acetate$	300 W Xe lamp	CO: 115.26 μ mol g ⁻¹	[96]
ZnSe-BF ₄		$CO_2 + H_2O$ + ascorbic acid	Solar light simulator	CO: 2.38 mmol g^{-1}	[97]
MAPbI ₃ @PCN-	221(Fe _{0.2})	CO ₂ + H ₂ O + ethyl acetate or acetonitrile	300 W Xe lamp (400 nm filter)	CO: 1559 μ mol g ⁻¹	[98]
Single-atom materials					
Pt/TiO ₂ -Ti	₃ C ₂	$CO_2 + H_2O$	300 W Xe lamp (AM 1.5 filter)	CO: 20.5 μ mol g ⁻¹ h ⁻¹	[99]
Er1/CN-N	Г	$CO_2 + H_2O$	300 W Xe lamp (420 nm filter)	CO: 47.1 μ mol g ⁻¹ h ⁻¹ CH4: 2.5 μ mol g ⁻¹ h ⁻¹	[100]

TABLE 2 (Continued)



FIGURE 4 (a) (i) SEM and STEM of TiO₂. Yield rate of products (ii) and selectivity (iii) on TiO₂. (iv) GC-MS spectra of TiO₂. Reproduced with permission: Copyright 2020, Elsevier.^[62] (b) (i) SEM of ZnO/ZnS. (ii) CO yield of ZnO/ZnS with different contents. Reproduced with permission: Copyright 2023, John Wiley and Sons.^[66]

could increase the exposure ratio of the (100) face, thus promoting the C-C coupling of intermediates. GC-MS spectra also confirmed the C-C coupling of C_2H_5OH from CO_2 intermediates. TiO₂ (100) was able to convert CO₂ to C_2H_5OH at a rate 22 times greater than that of pure TiO₂ by controlling the crystal plane.

Heterojunction-type photocatalysts possess welldefined heterogeneous interfaces, tunable edges, and abundant active sites. Moreover, their built-in electric field facilitates the efficient separation of photogenerated carriers from holes. The Z-scheme heterojunction made of TiO₂ and WO₃, as constructed by Nguyen et al. exhibits a staggered band structure.^[63] When the Fermi level (E_f) between them is aligned, electrons will spontaneously transfer from TiO₂ to WO₃, forming an electron consumption layer and an electron accumulation layer between TiO₂ and WO₃, respectively. At the interface, TiO₂ carries a positive charge while WO₃ carries a negative charge. This can lead to energy band bending and a built-in electric field within the space charge layer, both of which promote electron transfer from the CB of WO₃ to the VB of TiO₂ through the interface, where they can recombine with holes. Compared with the type-II heterojunction structure, the Zscheme retains the relatively higher energy level of VB holes and CB electrons, thus preserving the higher redox ability of the photocatalyst. After a light exposure period, the CO yields of Z-scheme TiO_2/WO_3 (324.72 µmol g⁻¹) were about 3.2 times that of TiO_2 , and the CH_4 yields $(175.42 \,\mu\text{mol g}^{-1})$ were about twice that of TiO₂. Finally, to improve the product selectivity, the authors loaded Ag on the material's surface, and the final CO selectivity increased from 31.63% to 100%. Lu et al.^[64] prepared Zn₂Ti₃O₈/ZnTiO₃ heterojunction catalysts by hydrothermal synthesis. After 4 h of UV reaction, the CH₄ and CO yields of Zn2Ti3O8/ZnTiO3 were 0.56 and 3.68 μ mol g⁻¹, respectively, which is about twice that of pure Zn₂Ti₃O₈. Wang et al.^[65] prepared S-scheme TiO₂@ZnIn₂S₄ CSHS heterojunctions, and the composites CO2 reduction conversion was increased by 2.75 compared with single component TiO₂.

3.1.2 | Other metal oxides

Furthermore, various other metal oxides have found extensive utility in the realm of PCRR. For instance, Ma et al.^[66] constructed a hollow tubular Type-II ZnO/ZnS heterojunction material, as shown in Figure 4b (i) incident light could undergo multiple scattering or reflection within the cavity, enhancing light capture and utilization. Additionally, the shell facilitated shorter carrier transfer paths, enabling more efficient

migration of carriers to the catalyst surface, thereby enhancing their participation in the reaction. In the meantime, the Type-II heterojunction structure could effectively suppress the separation of carriers and promote PCRR. As shown in Figure 4b (ii), the reduction performance of the composites was significantly higher than that of the pristine ZnO and ZnS. The deposition of Pt nanoparticles on ZnO/ZnS exhibited higher PCRR performance, which was attributed to the fact that Pt nanoparticles could promote the formation of Schottky junctions, thus enriching the reactive sites and improving the carrier separation efficiency. Zhang et al.^[67] have prepared ZnO/ZnSe Type-II heterojunction material. The experimental results showed that the methanol yield was $1581.82 \,\mu mol/g_{cat}/h$, which was three times that of pure ZnO, attributed to the fact that the heterojunction structure was beneficial to increase the photogenerated electron migration rate and inhibiting carrier complexation, thus extending the photogenerated electron lifetime and improving the PCRR performance.

The conventional type-II heterojunction structure improves the electron-hole separation efficiency, but it also exhibits strong coulomb repulsion, hindering successive carrier migration between different components of CB/VB, thereby reducing the redox potential to some extent. In contrast, the redox ability of the S or Z-scheme heterostructure will be retained to the maximum size, as the built-in electric field and the curved energy band facilitate carrier separation and transfer.^[69] CsPbBr₂ has excellent visible light absorption properties, strong reducing ability, and stability. Meanwhile, Bi₂WO₆ is low cost, easy to synthesize, and possesses efficient oxidizing ability. By fully integrating the high reducing power of CsPbBr₃ and the excellent oxidizing potential of Bi_2WO_6 , the overall conversion of CO_2 and H_2O to CO(or other products) and O_2 can be efficiently facilitated; and the oxidizing power of Bi₂WO₆ can be utilized to continually oxidize the H₂O, which can continuously and stably provide protons for the reduction reaction. Jiang et al.^[68] successfully prepared Z-scheme heterojunction materials of CsPbBr₃/Bi₂WO₆. As depicted in Figure 5a, the direct Z-scheme heterojunction exhibited a larger contact interface and shorter charge transfer distance. Consequently, it eliminated the need for an electron mediator to act as a route for electron transport. A builtin electric field was created when CsPbBr₃ was in close proximity to Bi₂WO₆ because it caused band bending inside the space charge layer. The efficient carrier transport across the CB of Bi₂WO₆ was made possible by this electric field.

Oxygen vacancies (OVs) can reduce the band gap of semiconductors and provide defective energy levels to



FIGURE 5 (a) The structure of CsPbBr₃/Bi₂WO₆. Reproduced with permission: Copyright 2020, John Wiley and Sons.^[68] (b) Theoretical calculation model of BiWO₆. Reproduced with permission: Copyright 2021, American Chemical Society.^[70]

enhance light absorption, while also lowering the interfacial charge transfer energy barriers.^[101] OVs are rich in localized electrons and can act as active surface sites to activate CO_2 in oxygen vacancies to $\cdot CO^{2-}$ radicals, thus improving photocatalytic CO₂ conversion.^[102] Lu et al.^[70] obtained three different types of oxygen vacancies by controlling the reaction conditions, which were located on W-O-W, Bi-O-Bi, and Bi-O-W sites. Generating different types of OVs can reduce the band gap of Bi₂WO₆ to different degrees and have other effects on photocatalytic performance. Among them, V1 oxygen vacancies exhibit a significant performance in adsorbing visible light (Figure 5b). However, OVs were quickly filled or lost during the photocatalytic reduction process. Hence, Wang et al.^[71] added Cu to CeO_2 , which increased the OV concentration and prevented the OV from being occupied. Some unpaired d-orbital electrons are present in the oxides or hydroxides of Fe, Cu, and Sn, and they can form complexes with VB electrons to stabilize OV. Additionally, the oxides or hydroxides of these elements possess specific redox properties and can accept electrons in the photocatalytic reaction, which further stabilizes the OV.

3.2 | Carbon-based nanomaterials

Graphene is a two-dimensional honeycomb sheet crystal composed of carbon atoms arranged in sp² hybrid mode. The p orbitals perpendicular to the sp² hybrid plane of each carbon atom form a delocalized, large π bond

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shoulder-to-shoulder, which extends throughout the entire graphene plane.^[103] The particular structure of graphene results in several exceptional properties, including a large specific surface area,^[104] rapid electron migration rate,^[105] and a broad range of light absorption.^[1]

Currently, most photocatalysts have good light absorption ability only in the ultraviolet region, which limits their practical application. However, when combined with graphene, the range of light absorption can be broadened, making it an ideal component for improving the utilization of light energy by photocatalysts. Wang et al.^[106] used chemical vapor deposition (CVD) to deposit fewer graphene layers on the ZnO surface in situ. The absorption edge of the composite material is similar to that of the original ZnO, indicating that the addition of graphene does not change the band gap of ZnO, and can also improve visible light absorption of ZnO. As shown in Figure 6a, Bie et al.^[72] used spherical SiO₂ as a template to grow CdS shells on its surface. Following that, NG was produced utilizing pyridine as a raw material on the finished CdS/SiO₂ composite. To create NG/CdS, the SiO₂ template was finally removed, and this structure produced a sizable region of intimate contact between NG and CdS. The loaded monolayer NG broadens the photo absorption region of CdS, shortens the electron migration distance, promotes the carrier transfer and separation, and achieves a seamless contact between the photocatalyst and the co-catalyst.

Among all manmade materials, graphene has approximately the biggest specific surface area.^[107] The incorporation of graphene into photocatalysts can enhance their surface area, leading to an increase in the availability of reactive sites. These reactive sites of graphene can undergo p-p conjugation with CO₂, meanwhile promoting adsorption, while P-P conjugation can also activate CO₂ and enhance CO₂ reactivity. Wang et al.^[73] loaded NG on TiO₂ HS, as shown in Figure 6b (ii, iii), the specific surface area of TiO₂ increases with the addition of NG. Due to the Lewis acid–base interaction between CO₂ and N sites, TiO₂/NG HS has substantially greater CO₂ adsorption than TiO₂. The production of numerous pyridine N sites by NG makes it easier for CO₂ to be absorbed and activated. (Figure 6b (iv)).

Graphene oxide (GO) and reduced graphene oxide (rGO) are homologs of graphene that can be obtained by exfoliating graphite oxide.^[108] GO comprises graphenelike structures with random-sized aromatic regions separated by sp³ hybridized carbon atoms around the surface with hydroxyl and epoxy groups (Figure 7a). In contrast, hydrophilic groups such as carboxyl and aldehyde are mainly distributed on the GO edges.^[109] These functional groups are added, which causes a

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FIGURE 6 (a) NG/CdS preparation method and TEM image. Reproduced with permission: Copyright 2020, John Wiley and Sons.^[72] (b) (i) TiO₂/NG HS preparation method and TEM image. (ii) Nitrogen physisorption isotherms and (iii) CO₂ adsorption isotherms of TiO₂, TiO₂/G and TiO₂/NG. (iv) Reaction processes of NG formation with pyridine on the surface of SiO₂/TiO₂ spheres. Reproduced with permission: Copyright 2021, Chinese Journal of Catalysis.^[73]

disruption in the sp² bonding network and results in a variety of electronic energy states that enable GO to form band gaps and have semiconductor characteristics.^[110] Mu et al.^[74] prepared CsPbBr₃ combined with α -Fe₂O₃, as shown in Figure 7b, as an electron mediator for

visible-light-driven CO₂RR photocatalyst. The XPS test results showed that the Br (3d) peak of CsPbBr₃/USGO/ α -Fe₂O₃ underwent a positive shift of the C peak relative to USGO/ α -Fe₂O₃ and the negative change of the C peak relative to USGO/ α -Fe₂O₃, suggesting the existence of



FIGURE 7 (a) Modes of graphene, graphene oxide, and reduced graphene oxide. Reproduced with permission: Copyright 2015, Royal Society of Chemistry.^[109] (b) (i) Preparation method, (ii, iii) XPS spectrums, and (iv) Yield of CO of CsPbBr₃/USGO/ α -Fe₂O₃. Reproduced with permission: Copyright 2020, John Wiley and Sons.^[74]

interfacial chemical bonding behavior between the three components. This bonding behavior can considerably enhance the electron transfer rate between CsPbBr₃ and α -Fe₂O₃. The final CO yield of CsPbBr₃/USGO/ α -Fe₂O₃ was 73.8 μ mol g⁻¹ h⁻¹.

RGO has most of the oxygen functional groups removed, allowing for the restoration of the sp² bonding network. The resulting more extensive sp² bonding network improves electron conductivity, making RGO an extreme performance candidate for catalyst carriers and electron acceptors/traps. Tang et al.^[75] prepared an rGO-coated Ag/Cu₂O ternary catalyst (Ag/Cu₂O@rGO) using a water bath and gas bubble-assisted film reduction method. Ag NPs can enrich the photoelectrons of Cu₂O octahedral nanocrystals, while the RGO nanolayer on Ag/Cu₂O surface can improve the reactants' capacity for adsorption and activation. The photocatalytic experiment results demonstrate that Ag/Cu₂O@rGO exhibits outstanding photocatalytic performance.

Graphitic carbon nitride $(g-C_3N_4)$ is a vital constituent among these materials, as it is highly regarded as a promising nonmetallic n-type semiconductor photocatalyst. This is primarily attributed to its exceptional thermal and chemical stability, facile structural tunability, low cost, straightforward preparation, and distinctive two-dimensional layered structure. It is a linear polymer of triple homogeneous triazine formed by carbon and nitrogen interconnections, and the C and N atoms in its structure are hybridized with sp^2 to form a highly delocalized II-conjugated system with suitable absorption band edges and band gaps, which allows it to reduce CO₂ under excitation by sunlight.^[36,111] Wang et al.^[76] developed a strategy combining K and B co-doping and Nv to prepare $g-C_3N_4$ in the preparation of $g-C_3N_4$. Theoretically, each doping element would play a role in modifying the material's structural or electronic structure properties. In contrast, the co-doping of multiple elements can synthetically address the various

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limitations of g-C₃N₄, while vacancies can adjust the band gap of g-C₃N₄ and increase its active sites. The combination of elemental co-doping and the introduction of vacancies synergistically enhances the material's adsorption capacity for CO₂, consequently enhancing photocatalytic activity. The experimental results showed that the reaction of KBH-C₃N₄ without any hole trapping agent for 5 h yields of CH₄ and CO was 161% and 527% of the original C₃N₄, the effectiveness of co-doping and Nv synergism was proved, respectively.

3.3 | Metalorganic frameworks (MOFs)

MOFs are porous materials with topological structures formed by binding metal ions or clusters to multidentate organic linkers,^[112,113] and have found extensive applications in areas such as catalysis, sensors, carbon capture, drug delivery, and adsorption and separation of gases.^[14,114–123] Because of their large surface area, variable structural composition, high porosity, and pore volume, MOFs are considered potential materials for CO₂ reduction.^[124,125] Compared with traditional semiconductor materials, MOFs offer two key advantages in photocatalysis. Firstly, their porous structure provides more reactive sites, which promotes charge transport and CO₂ adsorption, ultimately reducing the electron-hole recombination and improving the reactivity. Secondly, MOFs can be combined with other materials to broaden their visible light absorption range. The resulting composite structure facilitates faster carrier transfer and separation, further enhancing their photocatalytic activity.

Presently, only a limited number of MOFs exhibit a consistent photo-response to visible light, while most MOFs can only respond to UV light, restricting their ability to utilize solar energy. Based on the highly designable structure of MOFs, the visible light absorption of MOFs can be enhanced by introducing specific chromogenic groups (amino, hydroxyl, porphyrin, etc.) into organic ligands. Wang et al.^[77] prepared CTU/TiO₂ composite material by using a one-pot method in which CuTCPP was introduced into the UiO-66 MOF while TiO₂ was grown in situ on the MOF. The addition of CuTCPP broadened the light absorption range of UiO-66 MOF, resulting in a considerable increase in the PCRR performances.

Modulation of metal ions in metal cluster junctions can improve CO_2 conversion activity. Dong et al.^[78] synthesized a PCN-250-Fe₃ material with a metal cluster junction of Fe^{II}Fe^{III} and open metal sites. By adjusting the species of the second metal ion (MII) in the metal cluster, the authors found that all bimetallic PCN-250-

 Fe_2M (M = Mn, Zn, Ni, Co) had superior catalytic activity and product selectivity than the monumental PCN-250-Fe₃, with the most significant product selectivity of PCN-250-Fe₂Mn, with CO_2 conversion ($CO_2 \rightarrow CO$ $86.04 \text{ mmol h}^{-1}$). The experimental and theoretical calculations showed that introducing MII promotes the migration of carriers to the active site and inhibits the production of hydrogen precipitation intermediates, thus improving the adsorption and activation of CO₂. Because of the high electron affinity of Ni, a series of NH-MIL-125-Ni/Ti with different Ni/Ti molar ratios were prepared by Chen et al.^[79] The experimental and computational results analysis showed that NH2-MIL-125-Ni1% exhibits excellent CO₂ conversion with CO product selectivity up to 98.6%. The influence of Ni²⁺ doping on the electronic environment of titanium-oxygen clusters has been shown to enhance the charge transfer behavior of organic ligands to titanium-oxygen clusters, leading to a reduced band gap, and improving the efficiency of PCRR.

Defects in crystals can change the electronic form of the material, so defect engineering is also one of the efficient methods to enhance the PCRR activity of MOFs. He et al.^[80] used acetic acid as a modifier to introduce defects on UiO-66 (Zr), as shown in Figure 8a. A significant EPR signal at g = 2.002 in UiO-66-6, which corresponds to Zr³⁺, proves that Zr defects are present in UiO-66-6. The presence of Zr defects can broaden the photo-response of UiO-66-6. The experimental results showed that the product rate of UiO-66-6 is 13.3 µmol $g^{-1}h^{-1}$, about 13 times higher than that of UiO-66-6, and the efficacy of the photocatalytic CO₂RR is improved by suitable structural flaws. Wang et al.^[126] synthesized a series of UIO-66-NH₂ with different degrees of ligand vacancies with missing bonding (ML) and missing cluster defects (MC). The ML-type UIO-66-NH₂-ML-100 with ligand vacancies had the best photocatalytic activity. At the same time, the MC sample had weakened light absorption and increased Eabs due to the lack of metal clusters in its dicarboxylic acid ligands, leading to a decrease in photocatalytic efficiency.

3.4 | Metal chalcogenides

Metal chalcogenides are typically composed of sulfur and one or more metal elements, and can be categorized as binary metal chalcogenides (such as CdS, ZnSe.), ternary metal chalcogenides (ScAlTe₃, CuInS₂, etc.), and multimetal chalcogenides, such as Cu₂ZnSnS₄.^[127] Among the many photocatalysts, metal chalcogenides have attracted much attention because of their suitable energy band structure, negative CB potential, high carrier mobility,



FIGURE 8 (a) Conceptual model diagram of FLPs and EPR spectra of UiO-66-0 and UiO-66-6. Reproduced with permission: Copyright 2022, American Chemical Society.^[80] (b) (i) Preparation flowchart of 3DOM CdSQD/NC. (ii) UV-vis DRS spectra. (iii) Gas production rate and selective under various reaction conditions. (iv) Stability tests. Reproduced with permission: Copyright 2023, John Willey and Sons.^[82]

wide photo-response range, and abundance of active sites.^[128] However, similar to other materials, single metal chalcogenides exhibit faster-photogenerated carrier complexation, which is unfavorable for PCRR. In addition, the accumulation of h^+ on the surface of metal chalcogenide photocatalysts initiates spontaneous

oxidation of the surface sulfide ions, rendering the metal sulfide materials prone to light-induced corrosion, which leads to photocatalyst deactivation, thereby limiting both the photostability and potential applications.^[129] To solve this problem, a variety of modification methods can be utilized to enhance the catalytic performance of metal

chalcogenide catalysts, like morphology control, surface modification, construction of heterojunctions with suitable semiconductor materials or co-catalysts, and defect engineering.

Since photocatalytic reactions usually occur on the surface of photocatalysts, photocatalytic performance and the morphological structure of the material are closely related, and one of the best ways to increase photocatalyst activity is thought to be through morphological modification.^[130] You et al.^[81] introduced lattice distortion by selecting SnS₂-SnO₂ pairs as building blocks for hollow multishell structures (HoMSs), providing additional catalytically active sites and improving the electron-hole-prone complexation challenge. The authors exploited the good electron transport ability of SnO₂, the excellent light absorption ability of SnS₂, and various properties of HoMSs to achieve a record CO₂ reduction activity with 100% product selectivity for CO and excellent CO photostability.

Wang et al.^[82] prepared CdS QD loaded on 3DOM NC (3D ordered macroporous N-doped C) to produce a 3DOM (CdSQD/NC) photocatalyst (Figure 8b). The combination of CdS QD and 3DOM results in CdSQD/ NC with abundant catalytic active sites, excellent carrier migration rate, wide light response range, and better stability. Under visible light irradiation, the apparent quantum yield of 3DOM CdSQD/NC in CO generation was 2.9%. Introducing O, S, or other anionic vacancies in semiconductor materials can improve photocatalytic performance. Cao et al.^[83] introduced Cu metal sites and S vacancies on the surface of CdS to improve the conversion rate of CO₂. The experimental results showed that the reaction energy barrier for dissociative adsorption of CO_2 molecules on the CuCdS surface is 2.18 eV, which is significantly lower than the CdS, demonstrating that Cu and S sites can co-regulate the electron distribution of CdS to reduce the dissociative absorption energy, and encourage contact between the reactants and the CdS surface. It is therefore concluded that the dissociative adsorption of CO₂ is easier when Cu metal sites and S vacancies coexist, which effectively improves the activity of photocatalytic CO₂ reduction.

Metal chalcogenide catalysts produce electrons and holes under light exposure, then migrate to the catalyst surface. which subsequently move to the catalyst surface. Nevertheless, if more holes form before being absorbed by electrons, surface ions oxidize, endangering the stability of the catalyst as well as its use. As a result, it's vital to limit surface hole growth and reduce interactions between holes and surface ions. As opposed to the construction of heterojunctions can change the migration direction of the holes to another material instead of leaving them on the surface. In the Z-scheme heterostructure system, photoelectrons produced by semiconductor A with lower CB compound with holes created by semiconductor B with higher VB, leaving electrons with higher reduction capacity and holes with higher oxidation capacity, effectively promoting charge separation, enhancing redox ability. Wang et al.^[84] constructed direct Z-scheme Bi₂O_{2.33}-CdS heterojunction materials. Bi₂O_{2.33}-CdS exhibited higher product selectivity, maintaining a stable yield even after four reaction cycles. The excellent PCRR performance and stability of Bi₂O_{2.33}-CdS were mainly due to the Z-scheme heterostructure, which provides more active sites, and shorter charge transfer distance, thereby facilitating the efficiency of charge transfer and separation.

3.5 | MXenes

MXenes are another new class of 2D transition metalcarbon/nitride materials after 2D nanomaterials, such as graphene, boron nitride, and transition metal disulfides. Because of their advantages of high electrical conductivity, large specific surface area, abundant surface terminations, and tunable band gap width, they have been widely employed in energy storage and conversion,^[131,132] medicine,^[133] sensors ^[134] and catalysis,^[135] and so forth. The general formula of MXenes is M_n $_{+1}X_nT_x$, M is the transition metal; usually, $n = 1 \sim 4$; X is carbon, nitrogen, or carbon-nitrogen element; Tx represents the functional group (e.g., -F, -Cl and -OH) attached to its surface during the preparation process.^[136,137] So far, MXenes have been reported in four different structural compositions: M₂XT_x, M₃X₂T_x, M₄X₃T_x, and $M_5X_4T_x$. Among them, $M_3X_2T_x$ is one of the first and most extensively studied MXene materials.^[138,139] For example, the CuInZnS-Ti₃C₂T_x photocatalyst prepared by Wang et al.^[140] can effectively degrade tetracycline in water and perform the photocatalytic reduction of CO₂. The negatively charged Ti_3C_2Tx affects the nucleation and growth process of CuInZnS, making the CuInZnS nanosheets thinner, with larger pore size, more prosperous active sites, and more vital CO2 adsorption capacity stronger and more favorable for CO₂ adsorption and dissociation.

As MXenes are not semiconductors, they cannot function directly as photocatalysts. However, they can be utilized as co-catalysts in combination with photocatalysts to improve their performance and efficiency.^[141] Due to the two-dimensional layered structure of MXenes with abundant active sites, strong metal conductivity, and extensive work function, they can promote charge transport and separation.^[142] The coupling with semiconductor photocatalysts facilitates the photocatalytic CO₂ reduction reaction and enables the photocatalyst to obtain better stability and reproducibility.^[141] Zhang et al.^[85] coupled Cs₂AgBiBr₆ and Ti₃C₂T_x by electrostatic self-assembly method to enhance the performance of PCRR. The experimental results showed that, the photocurrent of Cs₂AgBiBr₆/Ti₃C₂T_x was much higher than that of the pristine Cs₂AgBiBr₆, indicating that the addition $Ti_3C_2T_x$ inhibits the carrier complexation. Besides, the semicircular arc observed in the electrochemical impedance spectrum (EIS) of Cs₂AgBiBr₆/ $Ti_3C_2T_x$ diminished, indicating a decrease in the charge transfer potential resistance between Cs2AgBiBr6/ $Ti_3C_2T_x$. In summary, $Ti_3C_2T_x$ may increase the carrier lifetime and transmit electrons from Cs₂AgBiBr₆ to its surface for effective electron-hole separation, dramatically improving the photocatalytic performance of $Cs_2AgBiBr_6/Ti_3C_2T_x$ materials.

Along with these binary composites, Xiao et al.^[86] reported that Cu was loaded on the Ti₃C₂T_x surface and coupled with g-C₃N₄ via electrostatic self-assembly to form a Cu-Ti₃C₂T_x/g-C₃N₄ (Cu-TC/CN) ternary heterostructure photocatalyst. Cu, Ti₃C₂T_x acts as an electron channel and the interface between the two has great active sites. The optimized material yields 49.02 μ mol g⁻¹ CO after a four-reaction nine times the original $g-C_3N_4$. The benefits of bentonite (Bt) include a sizable specific surface area, low cost, and porous structure, and coupling it with semiconductor materials can lead to rapid charge separation.^[87] Therefore, Tahir et al.^[143] successfully prepared novel $g-C_3N_4/Bt/Ti_3C_2$ heterojunction by synthesizing Bt with g-C₃N₄ and Ti₃C₂ using HF etching method composites, The addition of Bt enhanced the CO selectivity of this composite.

So far, most 2D MXenes materials have been composited by phase selective etching of the A-layer from its corresponding layer structure MAX by HF, which is strongly corrosive and has a high hazard index, making it unsuitable for large-scale MXenes production. Therefore, Sun et al.^[144] reported a method to synthesize Ti_2CT_x by electrochemical etching in an aqueous HCl electrolyte. Compared with HF or LiF, this chemical etching method does not involve fluoride ions. The resulting MXene material obtained only -Cl, -O, and -OH terminal groups, which is more suitable for carrying out the large-scale production of MXenes in practical applications.

3.6 | Perovskites

Perovskites are multifunctional materials with many properties, such as piezoelectricity, ferroelectricity, and photoelectricity. They are ready to be widely used in

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photocatalysis because of their unique electronic structure and properties, tunable band gap, and good visible light response.^[145] The chemical formula of perovskites is ABX₃, where A is an alkaline earth or rare earth metal cation, B is a transition metal cation, and X is an anion with a small atomic radius.^[146]

CaTiO₃ (CTO) is the first perovskite material discovered by researchers, which is subsequently derived in various new forms, such as ABX₃ and A₄BX₆.^[147] The structure of perovskite materials can be adjusted to tune the band gap, allowing for tailored visible light absorption and potential suitable for specific photocatalytic reactions. In addition, such systems can form lattice distortions that facilitate tuning the photoelectric properties.^[146] different types and compositions of anions and cations will have extra energy band structures and optoelectronic properties. The physicochemical properties of perovskite materials can be adjusted by elemental substitution or doping, which changes their chemical composition and facilitates the tuning of material properties such as band gap and optical responsiveness.^[148,149] Therefore, by altering their morphology, structure, and composition, adding co-catalysts, or creating heterojunctions with other materials, perovskite materials can have their photocatalytic characteristics enhanced.^[148] Tayyebeh Soltani et al.^[88] investigated the effect of Ag-TMO_x dual co-catalyst and different loading methods on the photocatalytic performance of CTO. The experimental results showed that other loading methods affect the activity of various substances, for example, photo-deposition increases the activity of CO generation, while impregnation enhances the activity of H₂. Additionally, the various catalyst compositions affected the selectivity of the reduction products. Ag (Pd) CTO has excellent yield and selectivity. Ag (Pd) CTO has excellent performance with a CO generation rate of 7.31 μ mol h⁻¹ and a product selectivity of 96%. At the same time, the pristine CTO sample without any co-catalyst mainly promotes the cracking of water to generate H_2 and O_2 .

Perovskites halides have been shown to have great potential for optoelectronic applications such as cells,^[150] light-emitting diodes,^[151] sensors,^[152] and lasers^[153] due to their optimal band gap, high photoluminescence quantum yield, and narrow emission band. Besides, the high carrier mobility, low binding energy, and tunable band gap of metal halide perovskite materials enable them to play an essential role in PCRR.^[21] Compared with oxide perovskite or other semiconductor materials, halide perovskites suffer from slow charge separation, fast carrier complexation, and relatively weak light absorption. They are usually coupled with different semiconductor materials or co-catalysts, such as graphene, g-C₃N₄, and metal or metal complexes, to improve



FIGURE 9 (a) The preparation of CsPbBr₃@GDY. TEM (b), Photochemical properties test (c) and Photocatalytic performance test (d) of CsPbBr₃@GDY. Reproduced with permission: Copyright 2020, American Chemical Society.^[90]

these problems. Li et al.^[89] prepared Cu-doped bi-phase CsPbBr₃-Cs₄PbBr₆ composites. The experimental results showed that Cu/CsPbBr₃-Cs₄PbBr₆ produced considerably more CO and CH₄ than pure CsPbBr₃: 185.2 and 149.1 μ mol g⁻¹, respectively. much higher than that of pure CsPbBr₃. Furthermore, the CO₂ reduction efficiency of the Cu/CsPbBr3-Cs4PbBr6 nanotube was 4.2 times higher than that of the CsPbBr₃ nanotube, and the electron consumption rate was 303% higher than that of the CsPbBr₃ nanotube. In conclusion, metal doping effectively improves perovskite nanomaterials' photocatalysis and product selectivity. Su et al.^[90] used microwave synthesis to coat graphite-acetylene (GDY) on CsPbBr₃ (Figure 9a,b). GDY could improve the photocatalytic stability of CsPbBr₃ and promote hole transfer from CsPbBr₃ to GDY, thereby inhibiting carrier

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complexation. As shown in the photoelectrochemical performance test in Figure 9c, the PL lifetime of CsPbBr₃@GDY was significantly shorter than that of CsPbBr₃. At the same time, the photocurrent density was substantially more significant than that of CsPbBr₃ and exhibited a smaller radius in the EIS test. Besides, CsPbBr₃@GDY had an adsorption capacity that was 3.2 times greater than that of CsPbBr₃, demonstrating that the C=C structure, nonlocalized electrons, and widely dispersed pores may enrich CO₂ to the catalytic surface and improve CsPbBr₃'s ability to adsorb CO₂. According to the findings, CsPbBr₃@GDY-Co had a CO₂ reduction activity of 27.7 mol g⁻¹ h⁻¹, which was about 8 times more than that of pure CsPbBr₃ (Figure 9d).

However, due to the toxicity and instability of lead in halide perovskite, this type of photocatalyst cannot be

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mass-produced and used in practical applications. Therefore, many researchers have focused on developing safer and harmless lead-free halide perovskite materials. Li et al.^[21] prepared an environmentally friendly ZnSe-CsSnCl₃ heterojunction composite by electrostatic selfassembly method. CsSnCl₃ provided more catalytic sites for ZnSe-CsSnCl₃ heterojunction, and reduced the ratelimiting step barrier, improving photocatalytic performance. However, Sn chalcogenides were prone to rapid oxidation in the air, In contrast, Bi-based lead-free chalcogenides had better stability, suitable band gap structure, good light absorption, and promising potential in photocatalytic CO₂ reduction.^[154,155] Wang et al.^[91] prepared Z-scheme and type-II lead-free perovskites Cs₂AgBiBr₆@g-C₃N₄ (CABB@C₃N₄) heterojunction materials, the Z-scheme heterojunction material had excellent CH₄ yield and the activity is much higher than that of g-C₃N₄. In contrast, the type-II heterojunction material had ultrahigh CO product selectivity. And there was no significant change in CO₂ conversion after four photocatalytic reaction cycle tests, indicating that the two heterojunction lead-free perovskite materials had good stability. Bhosale et al.^[92] synthesized three Bi-based Pbfree perovskite materials, Rb₃Bi₂I₉, CsBi₂I₉, and MA₃-Bi₂I₉, using a top-down approach. The experimental results showed that the PCRR performances of the three materials exhibited $CsBi_2I_9 > Rb_3Bi_2I_9 > MA_3Bi_2I_9$. The CH₄ yield of CsBi₂I₉ was 14.9 μ mol g⁻¹, and the CO yield was 77.6 μ mol g⁻¹, 25 times higher than the TiO₂ CH₄ yield under the same experimental conditions.

3.7 | Plasma materials

Plasma NPs are attractive because of their superior light absorption in a large wavelength range (400~2500 nm). They are primarily precious metal nanoparticles (Au, Ag, and Cu, among others).^[156] These particles differ from other materials because their surfaces are enriched with many electrons, which can exhibit collective oscillations under the influence of interaction forces, that is, localized surface plasmon resonance (LSPR). LSPR effect occurs when the incident light frequency matches the vibrational frequency of the various metal nanoparticles (NPs) or metal-conducting electrons. The NPs or metals will strongly absorb photon energy and further cause electromagnetic field enhancement.^[157] This property has been used in various applications such as sensors, photovoltaic devices, and light detection.^[158-160] Metal nanostructures can enhance light absorption effectively and broaden the light response range by LSPR.^[161] The light-absorbable content and near-field distribution of LSPR depend primarily on the morphology, composition,

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and size of plasmonic nanomaterials.^[162] To date, many plasma materials have been used in the field of photocatalytic CO_2 reduction.

The nonradiative decay of LSPR can capture lowenergy photons, which in turn generate high-energy "hot electrons," the presence of which can lower the CO₂ activation barrier and enable kinetically challenging multielectron reaction pathways.^[93] However, the photocatalytic efficiency and selectivity of hot-electron-driven CO₂ reduction still need improvement, often limited by low efficiency, fast dissipation, low selectivity for hydrocarbon production, and so on. In contrast, embedding a suitable semiconductor into the plasmonic matrix coupling hotspot can suppress the fast relaxation of hot electrons. The heterogeneous interface region between the plasmonic nanostructure and the semiconductor may be rich in vacancies or defects due to lattice mismatch, which can serve as active sites to reduce CO_2 (Figure 10a). Therefore, Jiang et al.^[93] constructed a plasma Au/TiO₂/W₁₈O₄₉ heterostructure rich in active "hot spots" and investigated the effect of the new "hot spots" on PCRR. As shown in Figure 10b, the Au/TiO₂/ W₁₈O₄₉ is a sandwich-like substructure. The incident light can be concentrated or amplified in the "hot spot" region to promote the electron leap from Au and $W_{18}O_{49}$ to the high-energy surface plasma (SP) state of electrons and generate high-energy hot electrons; the CB transmission of hot electrons from SP to TiO₂ in the plasma component may be further improved by the semiconductor TiO₂ that lies in between. Such a "sandwich" construction can simultaneously make the hot electron production and transfer processes and light absorption more sensitive. In the in-situ IR spectrum (Figure 10d), the presence of three intermediate peaks, namely CH₂*, CH₃O*, and HCO₃*, indicated their involvement in the CH₄ formation pathway. Moreover, the theoretical calculation results showed that the reaction potential of CO* intermediates plus H to COH* intermediates conversion was lower than that of CO* desorption to CO at the two interfaces of Au/TiO₂ and W₁₈O₄₉/TiO₂ (Figure 10c,e), demonstrating that the heterogeneous interfacial region of Au/TiO₂/W₁₈O₄₉ contained a large number of double heterogeneous active sites, which was conducive to the simultaneous adsorption of CO* and H⁺, thereby promoting the successive protonation reactions of CO* to generate COH*/HCO* intermediates and ultimately CH₄. The analysis of the experimental results showed that the visible light absorption of Au/ $TiO_2/W_{18}O_{49}$ was much higher than that of Au/TiO₂ and W18O49 and had higher photocatalytic activity and selectivity (Figure 10f-h).

Despite the ease of operation of LSPR, the cost of noble metals needs to be lowered to achieve practical



FIGURE 10 (a) Plasma/semiconductor heterostructure design drawing. (b) Mechanism diagram of $Au/W_{18}O_{49}/TiO_2$. (d) In situ FT-IR spectra. The potential energy of (c) Au/TiO_2 and (e) $W_{18}O_{49}/TiO_2$ hetero-interface. UV-Vis spectra (f), CO yield (g), and CH₄ (h) of Au and Au/W₁₈O₄₉. different light intensities. Reproduced with permission: Copyright 2017, John Wiley and Sons.^[93]

applications on a large scale. Therefore, researchers have developed several low-cost materials that have LSPR effects, like MoO_{3-x} and WO_{3-x}, which LSPR effects can be used as another candidate material for photocatalytic CO₂ reduction.^[163] Xie et al.^[94] prepared plasmonic MoO_{3-x}-TiO₂ nanocomposites composites, and the reason for the broad absorption range of MoO_{3-x} in the visible region compared with MoO₃ is that the LSPR effect broadens the light absorption range of MoO₃. Furthermore, MoO_{3-x}-TiO₂-NP and MoO_{3-x}-TiO₂-NT exhibited a more robust optical response than MoO_{3-x} in the visible region. Finding alternatives to precious metals is a major challenge in designing plasma photocatalysts. TiN also exhibits LSPR phenomena at longer wavelengths in the near-infrared. It can achieve charge transfer through contact with other semiconductors, making it an up-andcoming alternative to noble metals. Zhu et al.^[95] doped nonmetallic plasmonic TiN NPs into g-C₃N₄ NSs,

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effectively increasing the charge transfer rate and photocatalytic activity and broadening the light absorption range. It should be noted that too excessive particle size leads to the loss of the equipartition excitations and the transformation of nanoparticles from plasmonic excitonic elements to electron-hole "complex sinks," leading to the reduction of photocatalytic activity. When TiN particles are too large and the laser wavelength is too long, they can hinder the CO_2RR and result in a decrease in material performance.

Energy can also be transferred from metals to semiconductors in a contactless manner, for example, through electromagnetic effect energy resonance. Induced dipoles of localized surface plasmas can move energy resonance to electron and hole pairs in semiconductors. Extremely high electromagnetic field strengths and resonant energy transfer processes can also excite surrounding semiconductors. Additionally to the enhancement of the electric field and the generation of hot electrons, metal NPs can promote photocatalysis through the photothermal effect, which leads to the enhancement of reducing properties.^[164]

3.8 | QDs

QDs are nanoscale semiconductor particles with specialized electronic structure, quantum, and surface effects, which consist of a small number of atoms and usually range in size from 1 to 10 nm.^[165,166] The size of QDs is much smaller than that of their macroscopic material counterparts, and these effects further give rise to the tunable bandgap and unique optoelectronic properties of QDs.^[167,168] There are many advantages in the application of QDs in photocatalysis, such as (1) The advantage of the adjustable band gap of QDs can make semiconductors that do not possess intrinsic catalytic activity become highly efficient catalysts; (2) The multiexciton generation and hot-electron injection of QDs can improve the utilization efficiency of high-energy photons; (3) The smaller the size of the QDs, the shorter the path of electrons migrating to the surface, which is conducive to charge separation, and small-sized QDs have a larger specific surface area and more surface active sites.^[165,169,170] It is worth noting that the stability of single QDs is poor due to surface excitons. Therefore, usually, researchers will build heterojunctions, surface modification, or encapsulation to improve the catalytic activity of QDs and the stability of the structure.

The Cd atoms in CdSe QDs have excellent CO_2 adsorption ability and enough active sites in PCRR, and Se has the properties of electron cloud exclusion and electron enrichment, which can passivate the vacancy traps on the surface of chalcogenide through strong bonding. Yin et al.^[96] combined CsPbBr₃ QDs and CdSe QDs to construct efficient 0D/0D heterojunction materials for photocatalytic CO₂ reduction. The CsPbBr₃/CdSe heterojunction not only can utilize the advantages of CsPbBr₃ QDs, such as strong redox capacity and high photo-utilization rate, but also improves the shortcomings of the two components, such as fast electron-hole complexation rate, insufficient active sites, and low stability.^[171-175] The results showed that the strong electronic coupling of Pb-Se and Br-Cd bonds exists between CsPbBr₃/CdSe type II heterojunctions, which can promote carrier migration to the surface. In addition, the abundant edge and corner sites unique to CdSe accelerated *CO generation through the formation of Cd-C₂O₄- adducts, which led to more robust CO₂ activation and efficient conversion of CO₂ to CO with a final CO yield of $115.26 \,\mu\text{mol g}^{-1}$. Sahm et al.^[97] modified ZnSe QDs with imidazole, and the imidazole ligand was able to stabilize the *CO intermediate and hinder the occurrence of HER competition reaction, thus improving the CO₂ conversion of ZnSe QDs. Wu et al.^[98] encapsulated CH₃NH₃PbI₃ QDs in PCN-221 (Fe_x) to obtain photocatalysts with higher stability, which had a linear CO yield at 80 h of reaction time with linear CO₂ conversion.

3.9 | Single-atom materials

In traditional nanocatalysts, the proportion of highly active atoms located on the surface of the material is relatively low, and it is difficult for its internal atoms to participate in the catalytic reaction, which is not conducive to maximizing the catalytic performance. Single-atom catalysts (SACs) formed by uniformly anchoring mononuclear metal precursors on the surface of nanocarriers have a large number of exposed atomically dispersed metal active sites, which theoretically possess the maximum atomic utilization, thereby significantly improving catalytic efficiency.^[176-178] Furthermore, SACs also exhibit a unique unsaturated coordination environment, which greatly enhances the catalytic activity.^[179] SACs have the advantages of both homogeneous and heterogeneous catalysts, and have been gradually used in the study of catalytic carbon dioxide reduction.^[180,181]

The integration of isolated metal single-atom sites is key to the regulation of cross-interface charge transport, which not only enhances charge separation and functioning as electron sinks to capture electrons, thereby reducing the distance of charge transport.^[100] Li et al. anchored Pt atoms onto TiO₂-Ti₃C₂ (Pt-SA/TT).^[99] The three-dimensional hierarchical structure of TiO₂-Ti₃C₂ not only provided a robust interfacial driving force but also established atomic-level charge transport channels for directional electron transfer. Pt single-atom sites play a dual role, not only efficiently capturing electrons to shorten charge migration, but also serving as active centers to adsorb and activate CO₂. With the synergistic effect of Pt single-atom sites and efficient charge separation in the three-dimensional hierarchical structure of Pt-SA/TT, the CO yield of Pt-SA/TT reached 20.5 μ mol g⁻¹ h⁻¹ with a selectivity of 96%, which is five times higher than that of pure TiO₂.

To avoid the migration and aggregation of single-atom structures, the metal loading of SACs is usually kept at a low level, while the reduction of active sites leads to a decrease in catalytic activity. Therefore, it is crucial to preparing SACs with adjustable metal dispersion density. Ji et al. introduced a novel synthetic approach based on atom-confinement and coordination strategy (ACC) to fabricate catalysts with a

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tunable dispersion density of Er single atoms.^[100] The authors immersed a melamine sponge as a nitrogen source in a precursor solution of Er and urea, then froze it using liquid nitrogen. The sponge's porous structure and high specific surface area provided ample space to store and confine the precursor solution. Simultaneously, the coordination N atoms of sponge and urea and the ultra-low temperature of liquid nitrogen, a large number of Er ions were dispersed and fixed within the sponge, limiting their random migration. After subsequent freeze-drying and annealing treatments, single Er atoms anchored on carbon nitride nanotubes ($Er_1/CN-NT$) catalyst were successfully prepared. The Er metal content was tunable by adjusting the amount of Er precursor. The $Er_1/CN-NT$ proved to have excellent photocatalytic CO_2RR performance.

4 | CONCLUSION AND OUTLOOK

Using solar energy to reduce CO₂ to chemical fuels that can be stored and utilized is a practical, green, clean, and efficient means to solve the energy shortage. However, CO_2 is an inert gas with a high activation energy barrier. The conversion pathway to other chemical fuel gases is more complicated and challenging to control for selectivity. Moreover, the reduction of gaseous CO_2 by photocatalysts involves multiphase catalysis, which makes mass transfer between multiphase states difficult. Interacting with photocatalysts can be challenging, especially since some photocatalysts can only be excited for catalytic reactions under UV irradiation. Additionally, the rate of electron transfer in the catalyst is two to three energy levels slower than the rate of electron-hole complexation as a result of the irradiative relaxing of excited state electrons to the ground state. While surface modification, construction of heterojunctions, elemental doping, defect engineering, and loaded co-catalysts have been employed to enhance photocatalytic performance, the practical application of photocatalytic CO₂ reduction still poses significant challenges.

This review summarizes recent applications of several types of photocatalysts for CO_2 reduction. The challenges associated with low efficiency, poor stability, and low activity of photocatalysts are discussed, including carrier recombination, hazardous intermediate products, lack of active catalytic sites, and poor visible light absorption. The key issue in photocatalytic CO_2 reduction is improving photoconversion efficiency. Currently, photocatalysts lack a direct driving force to promote electron transport and transfer, leading to only a small fraction of photogenerated electrons successfully separating and migrating to the catalyst surface for redox reactions. Most photogenerated charges are consumed through

nonproductive recombination, resulting in poor photocatalytic performance. Therefore, developing new semiconductor photocatalysts with good charge transfer and separation, high quantum efficiency, a wide photoresponse range, and high stability is essential.

Many studies have focused on increasing the rate of electron-hole separation using various methods, but there is still a need for more research on the synergistic interaction between piezoelectricity and photocatalysis to enhance separation. charge transport and Piezoelectricphotocatalytic energy primarily employs polarization fields to promote charge transport and separation through additional driving forces, such as mechanical stirring or ultrasonic vibration, thereby improving the photocatalytic efficiency.^[182] Piezoelectric photocatalysis can improve photocatalytic performance in two ways: (1) By regulating the polarization of individual piezoelectric semiconductors to improve efficiency. Under mechanical stretching or strain in asymmetric directions, the crystal structure of the piezoelectric material deforms, and the positive and negative charge centers within the material are displaced, leading to spontaneous polarization.^[183] As a result, positive and negative charges are generated at different surfaces, resulting in an internal electric field, which facilitates charge separation and lowers the Schottky potential barrier, which promotes rapid migration of photogenerated charges and reduces reaction energy consumption. At the same time, mechanical stress also accelerates mass transfer and enhances catalytic activity.^[183,184] The use of electric field polarization inside piezoelectric semiconductors is an effective method for separating carriers, which can cause electrons and holes to migrate to the material surface in contrary directions, thereby inhibiting electron-hole compound and thus enhancing photocatalytic activity.^[185] (2) By building heterogeneous structures with other semiconductor materials, metals, or nonmetals.^[186] Most piezoelectric materials do not possess visible light absorption well; combining piezoelectric materials with conventional semiconductors or noble/nonprecious metal nanoparticles can give them photocatalytic capabilities. The alternating piezoelectric potential of piezoelectric heterostructures generated by periodic mechanical stress under the simultaneous action of ultrasonic vibrations (or mechanical stirring) and light can prevent the polarization field from being influenced by photogenerated charges. Most importantly, built-in electric field induced by piezoelectric effect and interfacial electric field at the heterojunction interface can synergistically promote charge transfer and separation, resulting in excellent synergistic effects in piezoelectric photocatalytic systems.

Overall, piezoelectric synergistic photocatalysis has enormous potential in the realm of photocatalytic CO_2 reduction, and it is expected that more efficient and highly selective photocatalysts will be developed in the future to solve the problems of energy shortage and environment.

AUTHOR CONTRIBUTIONS

Shanyue Lu: Investigation; writing—original draft preparation. Shengwei Zhang: Investigation; writing original draft. Qi Liu: Investigation; writing—original draft. Wen Wang: Formal analysis. Ning Hao: Formal analysis. Yajun Wang: Writing—review and editing. Zhou Li: Writing—review and editing. Dan Luo: Conceptualization; writing—review and editing.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

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