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Highly selective semiconductor photocatalysis for CO2 reduction

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Over the past few decades, photocatalytic CO₂ reduction has remained a prominent and growing research field due to the efficient conversion of CO_2 to value-added chemicals. Among the various photocatalytic performances, product selectivity has garnered considerable attention, which is the focus of this review. Herein, we first introduce the general background of photocatalytic CO₂ reduction, then according to the sequence of the entire reaction process, the adsorption and activation of reactants, the formation and stabilization of intermediates, and the desorption of products are summarized. After introducing each of the above steps that could mediate the final products, several modification techniques to improve the product selectivity are highlighted, including noble metal decoration, metal and non-metal doping, vacancy engineering, facet engineering, composite construction, and hydroxyl modification. Finally, current challenges and opportunities of interest in this rich field are discussed.

10th anniversary statement

Journal of Materials Chemistry A is one of the most important journals that concentrates on material applications in energy and sustainability and covers a wide range of specific content. In past studies, we focused on advanced materials for photocatalysis, piezocatalysis and electrocatalysis, including hydrogen production, nitrogen fixation, CO₂ reduction and degradation of organic pollutants. Our research interests include designing efficient catalysts via morphology control, vacancy engineering, size adjustment and modification. The source of synthetic reagents can be either chemical reagents or solid waste. Making solid waste into catalysts can alleviate the environmental problems caused by waste residue disposal sites. Moreover, we also concentrate on the catalytic mechanism using advanced spectroscopic techniques. On the occasion of the tenth anniversary of Journal of Materials Chemistry A, we sincerely celebrate the 10th anniversary of Journal of Materials Chemistry A and look forward to making further progress with the development of the journal in the future.

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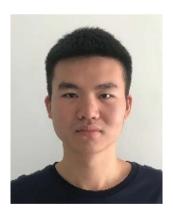
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1. Introduction

The industrial revolution has triggered the rapid development of science and technology,¹⁻¹⁰ however, the massive consumption of fossil fuels has caused a sharp increase in CO₂ concentration.¹¹⁻¹⁷ As of December 2020, CO₂ concentration in the atmosphere has reached 414.02 ppm, far higher than 270 ppm in the early 1800s, which is considerably higher than the safe value of atmospheric CO₂ concentration (*i.e.*, 350 ppm).¹⁸ As a consequence, a series of natural disasters, such as desertification, global warming and ocean acidification, have occurred frequently.¹⁹⁻²¹ Therefore, it has become an urgent issue to both alleviate the pollution caused by CO₂ and replace fossil fuels with clean and renewable energy sources.²²⁻²⁸

The photocatalytic conversion of CO₂ into hydrocarbon fuels of small molecular weight, such as CH₄, CH₃OH and C₂H₅OH, might kill two birds with one stone in terms of protecting the environment and saving energy.^{29–32} In the past several decades, tremendous efforts have been made toward CO₂ reduction initiated by solar light,^{33–38} and thus far, the activity of photocatalytic CO₂ reduction has greatly improved. Although the research and reports on the regulation of photocatalytic activity have been quite thorough, CO₂ reduction still has an obvious drawback, which is low selectivity and can be mainly attributed to the following reasons. First, as the energy barrier of CO₂ reduction to target products is comparable to that of hydrogen evolution (eqn (1)–(7) at pH 7 in aqueous solution), the side reaction (*i.e.*, hydrogen generation) is inevitable.^{39,40}

$$CO_2 + 2H^+ + 2e \rightarrow CO + H_2O \quad E^0 = -0.52 \text{ V vs. NHE} \quad (1)$$



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$$CO_2 + 2H^+ + 2e \rightarrow HCOOH \quad E^0 = -0.61 \text{ V vs. NHE} \quad (2)$$

$$CO_2 + 4H^+ + 4e \rightarrow HCHO + H_2O \quad E^0 = -0.51 \text{ V vs. NHE (3)}$$

$$CO_2 + 8H^+ + 8e \rightarrow CH_4 + 2H_2O \quad E^0 = -0.24 \text{ V vs. NHE (4)}$$

$$CO_2 + 6H^+ + 6e \rightarrow CH_3OH + H_2O \quad E^0 = -0.38 \text{ V vs. NHE}$$
(5)

$$CO_2 + 12H^+ + 12e \rightarrow C_2H_4 + 4H_2O$$
 $E^0 = -0.34 \text{ V vs. NHE}$ (6)

$$2H^+ + 2e \rightarrow H_2 \quad E^0 = -0.42 \text{ V vs. NHE}$$
 (7)

Thus, CO_2 reduction exhibits limited selectivity in aqueous solutions due to the critical challenge of overcoming the competition with the hydrogen evolution reaction (HER). In addition, the reduction potentials of converting CO_2 to different products are similar (eqn (1)–(6)).⁴¹ This phenomenon results in an undesirable mixture of products, which is hard to separate and utilize. Therefore, the improvement in selectivity is of key importance for photocatalytic CO_2 reduction.^{42–45}

This review aims to summarize recent impressive developments in the highly selective photocatalytic CO_2 reduction. After a brief discussion that motivates the research on high product selectivity, the reaction mechanism of photocatalytic CO_2 reduction is introduced to better understand the obstacle of reaction selectivity and the specific steps involved in the entire photocatalytic procedure. Then, the promotion of selective reaction at different reaction stages is summarized, including the adsorption and activation of reactants (*i.e.*, CO_2 adsorption



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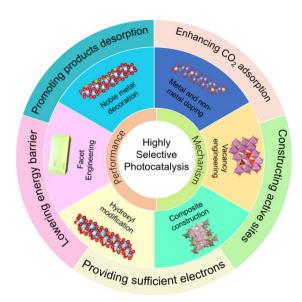


Fig. 1 Schematic illustration of photocatalyst modification and mechanisms in this review.

¹and H₂ evolution inhibition, electron supply and others), the formation and stabilization of intermediates (i.e., the formation energy of crucial intermediates and stability of intermediates), and the desorption of products. Particularly, modification methods of photocatalysts to boost selective reactions are discussed, including noble metal decoration, metal and non-metal doping, vacancy engineering, facet engineering, composite construction, hydroxyl and ion modification and other decoration techniques (Fig. 1). Lastly, a perspective on the challenges and future research directions of photocatalytic CO2 reduction possessing enhanced photocatalytic selectivity is proposed.

Mechanism of photocatalytic CO₂ reduction

Specific reaction processes of photocatalytic CO2 reduction are displayed in Fig. 2. Under light irradiation, the semiconductor photocatalyst absorbs photons. If the photon energy is equal to or larger than the band gap (E_g) of the photocatalyst, electrons and holes of the semiconductor are generated. The photogenerated electrons and holes then migrate to the surface of the photocatalyst.46 Photogenerated electrons are capable of reduction reactions that reduce CO2 on the surface of the semiconductor be reduced, while the holes oxidize H₂O to O₂. Photo-excited electrons and holes are prone to recombine both during the migration to photocatalyst surface and after reaching the surface, which significantly reduces the photocatalytic efficiency. Some parameters affect the reaction selectivity, including the reduction potentials of CO2 to products, the adsorption and desorption of different substances (i.e., CO₂, intermediates and products), and the utilization efficiency of photogenerated electrons.

The standard reduction potentials of CO2 are summarized in eqn (1)-(6) and eqn (8).47 As shown in eqn (8), CO2 - formation

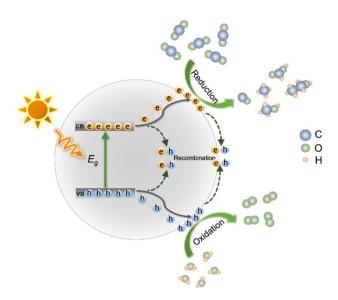


Fig. 2 Schematic illustration of photocatalytic CO₂ reduction.

through the single-electron reduction of CO₂ is unfavorable due to its very negative redox potential (i.e., -1.90 V vs. NHE).

$$CO_2 + e^- \rightarrow CO_2^{-}$$
 $E^0 = -1.90 \text{ V vs. NHE}$ (8)

Therefore, multi-proton-assisted CO₂ reduction reactions are prone to occur, possessing a relatively low thermodynamic barrier and bypassing the formation of CO₂ '- (eqn (1)-(6)).⁴⁸ From a thermodynamic point of view, the potentials of CO2 reduction (eqn (1)-(6)) are comparable to the potentials of hydrogen evolution (eqn (7)), which leads to a large amount of H₂ as the by-product. 49 According to the less negative redox potentials, it seems that the photoconversion of CO2 to CH3OH and CH₄ is more favorable than the H₂ evolution ([eqn (4)], [eqn (5)] and [eqn (7)]). Nevertheless, the requirement of more electrons to accomplish highly selective formation of CH₃OH and/ or CH₄ rather than H₂ is a great challenge.⁵⁰ Therefore, in order to realize the highly selective photoconversion of CO2, the photocatalysts should be carefully designed to suppress H2 evolution. In addition to the interference of H₂, the small differences between the thermodynamic potentials of different CO2 reduction products also make it tough to obtain single desirable products.40

Typically, the photocatalytic CO₂ reduction process involves three major steps: (i) the chemical capture and adsorption of CO2 on the surface of the photocatalyst; (ii) activation and breaking of C-O bonds and the formation of C-H bonds via electron transfer and proton migration; (iii) the configuration rearrangement of products and desorption from the photocatalysts.⁵¹ Each reaction step can be regulated by modifying photocatalysts or reaction conditions. In step (i), if the CO2 adsorption is enhanced and H2O adsorption is inhibited, the efficiency of CO₂ reduction will be largely increased and the H₂ evolution will be reduced. 52 Similarly, in step (ii), to obtain the products such as CH₄, CH₃OH and C₂H₄, a mass of electrons is needed. Thus, a sufficient electron supply and proper

suppression of electron-hole recombination are beneficial for their generation.⁵³ During the configuration rearrangement and intermediate conversion process, the formation and stabilization of crucial intermediates determine the direction of the subsequent reactions, promoting the selective generation of the target products. Finally, the easy desorption of obtained products can further enhance the selectivity.

3. Typical methods to enhance the selectivity and mechanism

Diverse strategies, including noble metal decoration, metal and non-metal doping, vacancy engineering, the exposure of highly active crystal facets, construction of complex materials, surface modification, morphology control and other methods, have been explored to manipulate the selectivity of the photocatalytic CO2 reduction. These techniques significantly increase the selectivity in terms of kinetics, adsorption and desorption capacity, electron supply, and intermediate stability. Diverse modification methods will affect different steps of CO2 reduction. Oxygen vacancies, noble metal and non-metal particles can not only affect the adsorption of CO2 but can also act as electron sinks, providing sufficient electrons for products. Composite construction, which can improve the CO₂ capture capability, also facilitates efficient photo-excited electron transfer and accumulation. Morphology control and facet engineering mainly affect the adsorption and desorption process during CO₂ reduction. We will introduce typical methods in the following sections. However, most of the work only briefly explains the reasons for the improvement of selectivity, rarely involving the essential reasons. The modified highly selective photocatalysts are listed in Table 1.

3.1. Adsorption and activation of reactants

3.1.1. CO₂ adsorption and H₂ evolution inhibition. As mentioned in Section 2, the hydrogen evolution is one of the main competing reactions for CO2 reduction, which could remarkably decrease the efficiency and selectivity of CO2 reduction. 49,80 Therefore, whether the catalysts tend to capture CO2 molecules or H2O and whether electrons tend to combine with CO₂, H⁺ or hydroxy groups from water molecules significantly affect the final products.46 As a consequence, CO2 adsorption is crucial to improve the selectivity. Here, we have summarized some special sites, including noble metal particles, oxygen vacancies and hydroxyl groups, which can effectively adsorb CO2 molecules and initiate rapid CO2 reduction reactions.46,72,81,82 Moreover, on exposing expected crystal planes and constructing composite structures, active sites can be provided for the preferential adsorption and conversion of CO₂ molecules, suppressing the H2 generation.83

For example, nearly 100% selective CO generation was achieved on the surface of spindle-like oxygen-vacancy rich (Vorich) Pt–Ga₂O₃ (Fig. 3a).⁸¹ The oxygen vacancies served as the main sites for CO₂ adsorption.⁸¹ Meanwhile, the hydrogen formed on Pt nanoparticles in the process of photocatalytic water splitting could quickly reduce the adsorbed CO₂.⁸¹ Besides

Pt, other noble metals also showed similar effects. After anchoring Au–Pd alloy on the $\{101\}n$ facets of TiO₂, the Au–Pd alloy provided abundant sites for CO₂ adsorption and activation.⁷³ Remarkably, the optimal sample achieved a high selectivity of 85% for hydrocarbons (71%: CH₄, 14%: C₂H₄ and C₂H₆, Fig. 3b).⁷³

Some special groups are also capable of the adsorption and activation of CO₂. For instance, the –OH groups on the Cu₂O surface facilitated the selective catalytic CO₂ reduction by suppressing the hydrogen evolution. He also sides, in the noble-metalfree SiO₂–TiO₂ system, the enhanced CO₂ photoreduction selectivity was assigned to the rational hydrophobic modification of the TiO₂–SiO₂ surface by replacing Si–OH with hydrophobic Si–F bonds. This kind of modification changed the hydrophilicity and hydrophobicity of the photocatalyst surface and thus mediated the reaction process. This improved selectivity was attributed to the efficient CO₂ adsorption, triggering efficient CO₂ photoreduction.

Different crystal faces possess different CO₂ adsorption capacities. So ZnO nanomaterials with a large ratio of {0001} facets could enhance the CO production selectivity and the exposed facets were terminated with a high density of oxygen atoms. Therefore, oxygen vacancies were prone to form on the surface of ZnO. These vacancies could preferentially capture CO₂ molecules and work as reduction sites for CO₂. As a consequence, the CO molecules could be produced as the main products. In addition, BiOBr nanosheets exposing {001} facets were successfully synthesized in the presence of nitric acid. Compared to the BiOBr nanosheets prepared in the absence of nitric acid (BiOBr-0), the {001} facets-dominated BiOBr nanosheets exhibited more efficient CO₂ absorption and activation, selectively converting CO₂ to CO (Fig. 3c). So

The adsorption and activation capacity can also be improved by changing the structure of the material. Typically, $g-C_3N_4$ -based composite catalysts display strong CO_2 capture ability, which promotes the generation of CO rather than H_2 . 88

The selectivity enhancement of CO production also appeared in other semiconductor composites, such as LDH/Ti₃C₂ and Ga₂O₃/ZnGa₂O₄.46,67 Taking the Ga₂O₃/ZnGa₂O₄ catalyst as an example, the ZnGa2O4 layer could suppress the reduction of H⁺.67 The proposed mechanism is displayed in Fig. 3d. Since a large number of active sites on the surface of Ga2O3 could capture and reduce H+, the main reaction on the surface of Ag-Ga₂O₃ was hydrogen production (Fig. 3d).⁶⁷ After the growth of the ZnGa₂O₄ layer on the surface of Ga₂O₃, it blocked the active sites that are conducive to hydrogen evolution. Therefore, with the amount of ZnGa₂O₄ increasing from 0.1 to 10.0 mol%, the generation of H₂ was significantly suppressed. Finally, CO generation with nearly 100% selectivity was achieved over Ga₂O₃/ZnGa₂O₄ heterostructures (Fig. 3e).⁶⁷ Crafting ultrathin two-dimensional semiconductor nanomaterials is another popular technique for achieving high photocatalytic selectivity.89-92 Bai found that compared with the bulk counterpart, the ultrathin Bi₄O₅Br₂ (Bi₄O₅Br₂-UN) exhibited increased CO generation of over 99.5% through an enhanced CO₂ adsorption capacity (Fig. 3f).⁷²

Review

Table 1 Summary of highly selective photocatalysts for CO₂ reduction

Photocatalyst	Light source	Experimental conditions	Main products and selectivity	Ref.
Ag/CaTiO ₃	100 W Hg lamp	0.3 g of catalysts, NaHCO ₃ aqueous solution (1.0 M)	CO (180 μmol g ⁻¹ h ⁻¹), 94%	54
TiO ₂ -Pd@Au	300 W Xe lamp	15 mg of catalysts, CO ₂ and 5 mL H ₂ O	CH ₄ (48.2 μmol g ⁻¹ h ⁻¹), 93.5%	55
(Pt/TiO ₂)@rGO	300 W Xe lamp	Certain amounts of catalysts, CO ₂ and 2 mL H ₂ O	CH ₄ (41.3 μmol g ⁻¹ h ⁻¹), 99.1%	56
${\rm Pt@Ag-TiO}_2$	350 W Xe lamp	Certain amounts of catalysts, CO ₂ and Na ₂ SO ₄ aqueous solution (0.5 M)	CH ₄ (160.3 μmol g ⁻¹ h ⁻¹), 87.9%	57
Pt/TiO ₂	300 W Xe lamp	50 mg of catalysts, CO ₂ and 50 mL H ₂ O	CH ₄ (150.04 μmol g ⁻¹ h ⁻¹), nearly 100%	58
N-doped C dot/CoAl-LDH/ C ₃ N ₄	300 W Xe lamp	50 mg of catalysts, CO_2 and 300 μ L H_2O	CH ₄ (25.69 μmol g ⁻¹ h ⁻¹),	59
N-TiO ₂	200 W Hg lamp	Gas mixture of CO ₂ and H ₂ with a ratio of 1:1	CO (56.30 μmol g ⁻¹ h ⁻¹), 96.3%	60
Cu-TiO ₂	300 W Xe lamp	60 mg of catalysts, 1.60 g NaHCO ₃ and 5 mL H_2SO_4 solution (5.0 M)	CH ₄ (150.9 μmol g ⁻¹ h ⁻¹), 85%	61
WO_{3-x}	UV-Vis-NIR light	5 mg of catalysts, CO ₂ and 0.2 mL H ₂ O	C_2H_4 (61.6 μ mol $g^{-1} h^{-1}$), 89.3%	62
${\rm BiMoO_6}$	300 W Xe lamp	50 mg of catalysts, 1.50 g NaHCO ₃ and 5 mL H_2SO_4 (4 M)	CH ₄ (2.01 µmol g ⁻¹ h ⁻¹), 96.7%	63
Defective CeO ₂	300 W Xe lamp	50 mg of catalysts, CO_2 and 0.2 mL H_2O	CO (7 μ mol g ⁻¹ h ⁻¹), nearly 100%	64
g-C ₃ N ₄ /FeWO ₄	Visible light ($\lambda > 420 \text{ nm}$)	40 mg of catalysts, CO ₂ and H ₂ O	CO (6 μmol g ⁻¹ h ⁻¹), 99%	65
NiAl-LDH/Ti $_3$ C $_2$	300 W Xe lamp	100 mg of catalysts, CO ₂ and 0.4 mL H ₂ O	CO (11.82 μmol g ⁻¹ h ⁻¹), 92%	66
Ag-loaded Ga ₂ O ₃ /ZnGa ₂ O ₄	400 W Hg lamp	1 g of catalysts, CO ₂ and 1 L H ₂ O	CO, nearly 100%	67
Pt/HAP/TiO ₂	300 W Xe lamp	20 mg of catalysts, CO ₂ and 40 mL H ₂ O	CH ₄ (4.64 μmol g ⁻¹ h ⁻¹), 99.1%	68
$C_3N_4/Pd_9Cu_1H_x$	Visible light	15 mg of catalysts, CO ₂ and H ₂ O	CH ₄ (1.20 μ mol g ⁻¹ h ⁻¹), nearly 100%	69
$\mathrm{Cl}^-/\mathrm{Bi}_2\mathrm{WO}_6$	300 W Xe lamp	20 mg of catalysts, CO ₂ and H ₂ O	CH ₄ (3.21 μmol g ⁻¹ h ⁻¹), 94.98%	70
Pt@h-BN	300 W Xe lamp	10 mg of catalysts, CO ₂ and 0.5 mL H ₂ O	CH ₄ (184.7 μ mol $g_{(Pt)}^{-1} h^{-1}$), 99.1%	71
Ultrathin Bi ₄ O ₅ Br ₂	300 W Xe lamp	20 mg of catalysts, CO ₂ and H ₂ O	CO (31.565 μmol g ⁻¹ h ⁻¹), 99.5%	72
Au–Pd alloying loaded TiO ₂	UV light	10 mg of catalysts, CO_2 and H_2O	Hydrocarbon fuels (CH ₄ , C ₂ H ₄ , and C ₂ H ₆) (25.06 μ mol g ⁻¹ h ⁻¹), 85%	73
V-defective BiVO ₄	300 W Xe lamp	100 mg of catalysts, CO_2 and H_2O	CH ₃ OH (398.3 μ mol g ⁻¹ h ⁻¹)	74
Defective C ₃ N ₄	350 W Xe lamp	100 mg of catalysts, CO ₂ and H ₂ O	CH ₄ , CH ₃ OH, and CH ₃ CH ₂ OH (12.07 μ mol g ⁻¹ h ⁻¹), 91.5%	75
W-doped g-C ₃ N ₄	300 W Xe lamp	5 mg of catalysts, CO_2 and H_2O	CH ₄ and C ₂ H ₄ (11.91 μ mol g ⁻¹ h ⁻¹), 83%	76
Cu _x In ₅ S ₈ –Cu _y Se	300 W Xe lamp	10 mg of catalysts, CO ₂ and H ₂ O	CH ₃ OH (5.25 μ mol g ⁻¹ h ⁻¹), about 100%	77
Microwave-synthesised carbon-dots	300 W Xe lamp	10 mg of catalysts, CO ₂ and H ₂ O	CH ₃ OH (13.9 μmol g ⁻¹ h ⁻¹),	78
C ₃ N ₄ -supported CoS	300 W Xe lamp	10 mg of catalysts, CO ₂ and H ₂ O	CH ₃ OH (97.3 μmol g ⁻¹ h ⁻¹), 87.2%	79

In summary, by constructing composites, introducing metal sites and constructing oxygen vacancies, the adsorption and activation capabilities of photocatalysts in the first step of the ${
m CO_2}$ reduction reaction can be significantly improved. Therefore, the target reaction occurs instead of the competitive hydrogen evolution. However, in previous reports about the first

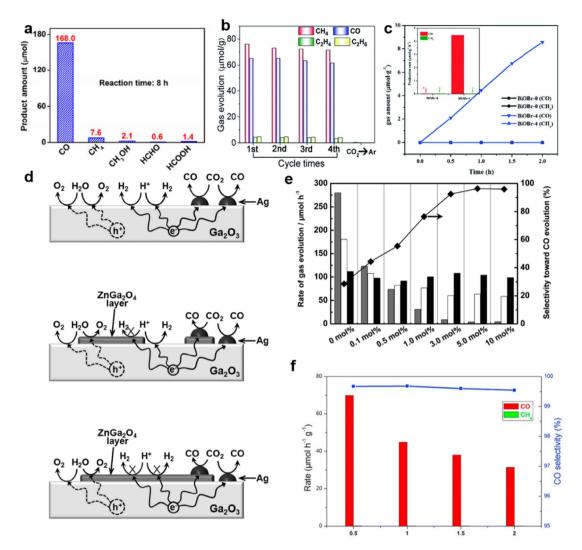


Fig. 3 (a) The amount of products over V_O -enriched Pt-Ga₂O₃ after irradiation for 8 h. Reproduced with permission from ref. 81 copyright 2018 Springer. (b) Photocatalytic yield and stability of Au-Pd-alloy-decorated TiO₂. Reproduced with permission from ref. 73. copyright 2019 Royal Society of Chemistry. (c) Production rates of CH₄ and CO over BiOBr photocatalysts under Xe light irradiation. Reproduced with permission from ref. 83 copyright 2017 Royal Society of Chemistry. (d) A proposed mechanism for the photocatalytic conversion of CO₂ in H₂O over Aq-loaded Ga₂O₃, Aq-loaded Zn-modified Ga₂O₃ with a low Zn content, and Aq-loaded Zn-modified Ga₂O₃ with a high Zn content. (e) Evolution rates of CO (black), O₂ (white), and H₂ (gray) in the photocatalytic conversion of CO₂ over Ag-loaded ZnGa₂O₄-modified Ga₂O₃ containing different amounts of ZnGa₂O₄. Reproduced with permission from ref. 67. Copyright 2016 Royal Society of Chemistry. (f) Evolution rates and selectivity over $Bi_4O_5Br_2$ and $Bi_4O_5Br_2$ -UN under UV-vis illumination. Reproduced with permission from ref. 72. Copyright 2017 Elsevier.

step of the CO₂ reduction reaction, there is a lack of the selective generation of different carbon reduction products. In addition, how CO2 adsorption mediates carbon products needs to be further explored.

3.1.2. Electron supply. The formation of high-value-added products such as CH₄ is usually a multi-electron reaction. In order to generate target products via multi-electron reactions, the accumulation of sufficient photogenerated electrons is necessary. Noble metals, non-metallic impurities and vacancies of photocatalysts can act as electron sinks, providing sufficient electrons for selective products.53,57,93-96 Therefore, by constructing special nanostructures, electrons can be enriched in the target area to achieve selective reactions.

Pan et al. reported that after decoration by Pt nanoparticles, LaPO₄ reached a 5.6 times enhancement in CH₄ yield compared to pure LaPO₄ (Fig. 4a).⁵³ The selectivity of CH₄ production increased from the original 58.6% to 100% when the amount of modified Pt nanoparticles increased from 1 wt% to 3 wt% (Fig. 4a).⁵³ In this research, Pt nanoparticles functioned as the photogenerated electron sink, which thus accelerated the eightelectron reduction of CO2 to CH4.53 This mechanism was proved in another report, where Pt/Cu2O nanoparticles trapped sufficient photogenerated electrons and ensured the multielectron photocatalytic reactions to form CH₄ (Fig. 4b-d).⁹⁷ It is noteworthy that the electron sink effect of Pt also exists in other catalysts. The selectivity of CH₄ formation was improved when Pt@Ag core@shell structures were decorated on TiO2

nanoparticles (Fig. 4e).57 The Pt core served as a sink for photogenerated electrons, and the Ag shell suppressed the competitive photocatalytic water-splitting process. By tuning the ratio of Pt to Ag, 1.95 wt.% Pt@Ag_{1.0}-TiO₂ achieved the outstanding photocatalytic performance with a CH₄ formation rate of 160.3 mmol g⁻¹ h⁻¹ and a CO₂ conversion selectivity of 87.90%.57

Besides noble metals, doped common metals could also perform as electron traps and active sites for the highly selective CO₂ photoreduction. 104,105 For example, Cu doping effectively provided TiO₂ with electron traps, leading to a higher methanol yield. 93,106 The Cu sites of ZnO/CuO_x-C (the abbreviation C stands for Cu doping) carbon nanofibers (CNFs), which worked as electron traps, could also generate enough electrons for CH₄ formation (Fig. 4f).99 Among ZnO-Cu₂O hybrid nanoparticles (ZnO@Cu₂O), Cu₂O cube-ZnO heterostructures (Cu₂O@ZnO), Cu₂O/ZnO nanocomposites (Cu₂O/ZnO) and Cu₂O/ZnO mixtures, ZnO/CuOx-C CNFs demonstrated the highest CH4 generation rate of 241.6 µmol h⁻¹ g⁻¹ with the selectivity of

 \sim 96% (Fig. 4g and h). 99 Besides the introduction of metallic Cu, highly selective CH₄ synthesis was achieved by introducing metal Mg.100 CO2 photoreduction rates of pure TiO2 and TiO2 decorated by different amounts of Mg are shown in Fig. 5a. Mg-TiO₂ promoted a large enhancement of electron trap sites, thereby ensuring sufficient electron supply for the selective reduction of CO2 to CH4.100 Moreover, the doping or co-doping of other metals, such as Mo and Ce, could improve the photocatalytic conversion selectivity of CO2 to high value-added products by increasing electron traps. 107,108 However, not all metals have the function of electron sink. Due to high CO2 adsorption, In-TiO2 nanoparticles achieved the highest CO selectivity of 94.39% with In doping of 10% (Fig. 5b) but with the limited electron supply, it was unable to achieve a high CH₄ vield. 101 Therefore, we need to select the appropriate metal to modify the photocatalyst according to the designed product target.101

The selective preparation of high-value-added products can be also achieved by creating oxygen vacancies.111 Therefore,

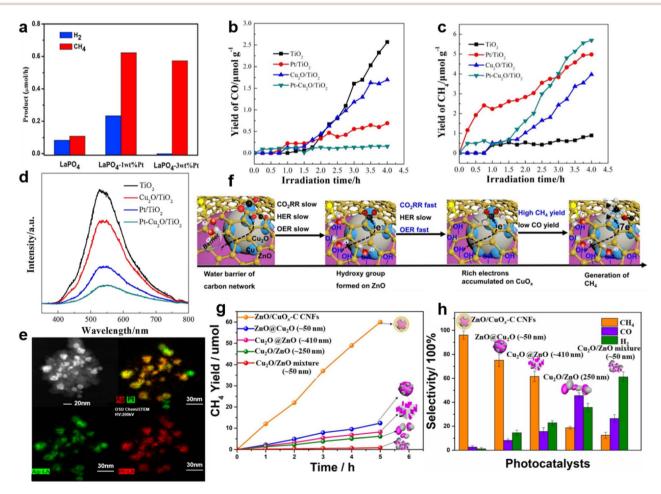


Fig. 4 (a) Generation rates of CH₄ and H₂ over the LaPO₄ and LaPO₄-Pt samples. Reproduced with permission from ref. 98 copyright 2015 Elsevier. (b) CO yields, (c) CH₄ yields and (d) PL spectra of TiO₂, Cu₂O/TiO₂, Pt/TiO₂ and Pt-Cu₂O/TiO₂. Reproduced with permission from ref. 97 copyright 2017 Elsevier. (e) STEM mapping images of Pt@Aq_{1.0}-TiO₂. Reproduced with permission from ref. 57 copyright 2018 Elsevier. (f) The proposed photocatalytic mechanism of highly selective CH₄ production over ZnO/CuO_x-C CNFs. (g) The CH₄ yield and (h) the product selectivity of ZnO/CuO_x-C CNFs, ZnO@CuO, Cu₂O@ZnO, ZnO/Cu₂O and Cu₂O/ZnO. Reproduced with permission from ref. 99 copyright 2021 Elsevier.

defect-rich $\mathrm{Bi_6Mo_2O_{15}}$ sub-microwires with abundant oxygen vacancies, which could capture sufficient photo-generated electrons, are favorable for the photocatalytic reduction of $\mathrm{CO_2}$ to $\mathrm{CH_4.^{93}}$ Oxygen vacancies and metal vacancies can act synergistically to jointly improve the reaction selectivity. 102 Both oxygen and metal Ni vacancies were detected in NiCo-layered double hydroxide hollow nanocages (HC-NiCo-LDH), and the introduction of vacancies could create a new defect level in the middle of the band gap, causing a decreased band gap and enhanced charge transfer of HC-NiCo-LDH (Fig. 5c); 102 this guaranteed enough photo-induced electrons to reduce $\mathrm{CO_2}$ molecules. 102 Finally, the $\mathrm{CH_4}$ selectivity was increased from 8.92% to 62.66%. 102

g- C_3N_4 -based semiconductor composites could also selectively obtain CH_4 or other fuels. Truc reported that compared with pure $Cu_2V_2O_7$ (*i.e.*, 0) and g- C_3N_4 (*i.e.*, 0), the

50Cu₂V₂O₇/50g-C₃N₄ photocatalysts possessed more active electrons in the CB of the g-C₃N₄. Enough electron supply of 50Cu₂V₂O₇/50g-C₃N₄ accomplished the selective generation of CH_4 (i.e., 1696 mmol g^{-1} cat. h^{-1}). Additionally, in the g- C_3N_4 / ZnO system, the electrons of ZnO recombined with the photogenerated holes of g-C₃N₄, thereby retaining the electrons with strong reduction capability in g-C₃N₄.¹¹⁵ Sufficient electrons in the CB of g-C₃N₄ boosted the conversion of CO₂ to CH₃OH.¹¹⁵ ZnO nanorod arrays@-carbon fiber (ZnO NA@CF) composites showed highly selective CH₃OH production during the photocatalytic CO₂ reduction. 116 Owing to the interaction between ZnO nanocrystals and carbon fiber, photo-generated electrons could transfer from ZnO to the surface of the carbon fiber, thus preventing the recombination of electron-hole pairs. 116 Photo-induced holes in the VB of ZnO reacted with water to produce O2 and H+, while CO2 molecules were

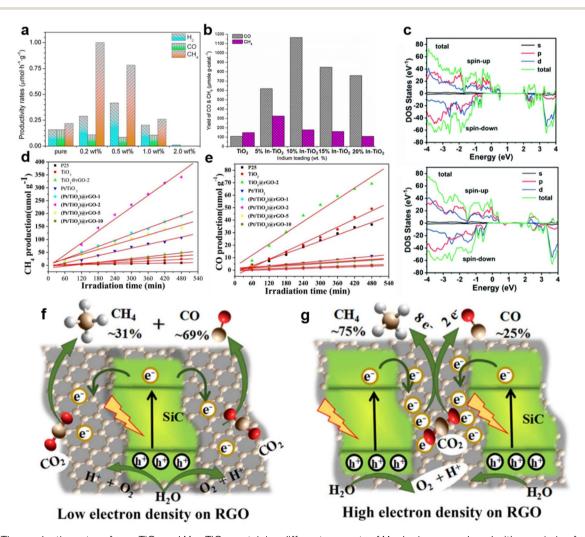


Fig. 5 (a) The production rates of pure TiO_2 and $Mg-TiO_2$ containing different amounts of Mg doping, reproduced with permission from ref. 100 copyright 2014 Elsevier. (b) The yield of products of $In-TiO_2$ with different amounts of In doping, reproduced with permission from ref. 101 copyright 2013 Elsevier. (c) Calculated total DOS (TDOS) and partial DOS (PDOS) plots of HC-NiCo-LDH without (upper) and with (lower) oxygen vacancies and Ni vacancies. Reproduced with permission from ref. 102 copyright 2018 Royal Society of Chemistry. (d) CH_4 production and (e) CO production over TiO_2 , Pt/TiO_2 , TiO_2 @rGO-2 and Pt/TiO_2)@rGO-P catalysts. Reproduced with permission from ref. 56 copyright 2018 Elsevier. A schematic illustration of the electron density-dependent CH_4 selective production over SiC/rGO heterojunctions with (f) low electron density and (g) high electron density on rGO. Reproduced with permission from ref. 103 copyright 2018 Wiley.

selectively reduced to CH₃OH by sufficient electrons on the carbon fiber. 116 rGO is another appealing photocatalyst that can accumulate electrons of high energy to accelerate CH4 generation via an eight-electron catalytic process.117 Bare rGO is not active for the photocatalytic conversion of CO₂ to CH₄ (ref. 56) but rGO-wrapped Pt/TiO2 ((Pt/TiO2)@rGO) photocatalysts achieved excellent selectivity (i.e., 99.1%) of CH₄ evolution (Fig. 5d and e).56 Pt nanoparticles in (Pt/TiO2)@rGO-n photocatalysts functioned as an accumulator for electron transfer in the TiO2-Pt-rGO ternary system.⁵⁶ Due to the strong electronwithdrawing capacity of the rGO shell, the photogenerated electrons could further transfer from Pt to rGO.56 Thus, the photo-generated electrons were transferred from TiO2 to Pt and finally to the rGO shell (i.e., $TiO_2 \rightarrow Pt \rightarrow rGO$). The photogenerated electrons accumulated on the rGO shell and subsequently reacted with the adsorbed CO₂ to produce CH₄.⁵⁶ The photo-excited electron transfer and accumulation process was also observed in SiC/rGO composites. 103 The electron density of the pure rGO surface was low. 103 In the SiC/rGO heterojunctions, the SiC served as the source of photogenerated electrons, while the rGO helped to quickly transfer energetic electrons for subsequent CO₂ reduction, resulting in a high CH₄ selectivity. 103

It is worth noting that by choosing a suitable ratio of SiC to RGO, a high electron density could be formed on the surface, thereby promoting the selective formation of CH₄ (Fig. 5f and g).103 Additionally, crafting semiconductor composites might enhance photocatalytic selectivity via inducing oxygen vacancies. 109 Devi reported that the considerable carbon reduction selectivity of the In₂O₃-2wt% rGO nanocomposite (i.e. CH₄ generation rate of 953.72 µmol h⁻¹ g⁻¹ with the selectivity of \sim 74%) could mainly be attributed to the induced oxygen vacancy defects by the addition of rGO (Fig. 6a-c). 109

The adjustment of the nanostructure and morphology of the materials can also change the accumulation of electrons, thereby facilitating the enhancement of photocatalytic performance in terms of selectivity. Pt-coated hexagonal boron nitride nanoreactors (Pt@h-BN) were synthesized by a two-step technique (Fig. 6d). 110 Among pure Pt, pure BN and the intermediate state BN before obtaining Pt-coated BN nanoreactors (Pt@IS-AB, middle part of Fig. 6d), Pt@h-BN with the Pt:B molar ratio of 1:3 (Pt@h-BN₃) demonstrated the best photocatalytic activity and achieved a nearly 100% selectivity of CO2-to-CH4 (Fig. 6e).110 It was revealed that the special nanostructure composed of Pt as the core and h-BN as the shell (Fig. 6f and g)

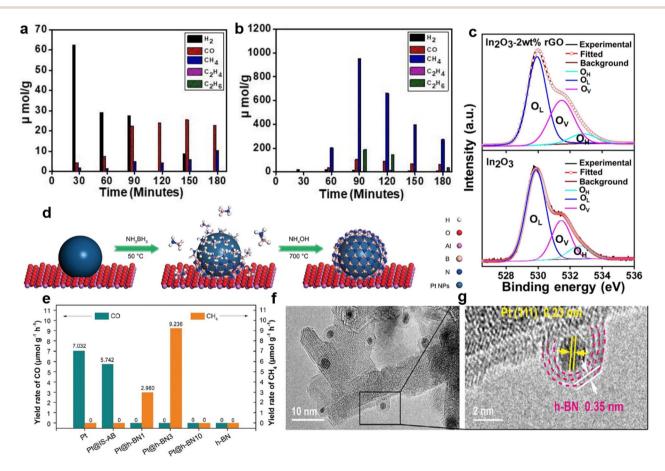


Fig. 6 Generation efficiency of various products over (a) In₂O₃ and (b) In₂O₃-2 wt% rGO. (c) High-resolution XPS spectra of O 1s of In₂O₃-2 wt% rGO nanocomposites (upper) and In₂O₃ nanostructures (lower). Reproduced with permission from ref. 109 copyright 2021 Elsevier. (d) Schematic diagram of the synthesis process of Pt@IS-AB and Pt@h-BN series catalysts originating from Pt. (e) The photocatalytic CO₂ conversion rate of Pt, Pt@IS-AB, Pt@h-BN series catalysts and pure h-BN. (f and g) HRTEM images of Pt@h-BN3. Reproduced with permission from ref. 110 copyright 2021 Wiley.

accelerated the electron mobility to produce the key intermediate CO²⁻ species on the surface of Pt@h-BN.¹¹⁰ Compared to pure BiVO₄, the lamellar BiVO₄ showed the selective generation of CH₃OH due to efficient electron capture to form CO₂·- radical anions.¹¹⁸ These provided researchers with a new method to construct highly selective photocatalysts by the delicate design of the architectures of photocatalysts.

Adequate electron supply is the most common mechanism to explain the selective reduction of ${\rm CO_2}$ to ${\rm CH_4}$ and other high-value-added products.

3.1.3. Others. As the active sites, metal ions, oxygen vacancies and metals loaded on the surface of photocatalysts are capable of the chemical conversion from CO₂ to specific products. Appropriate CO₂ adsorption together with efficient electron accumulation are proposed to cause high product selectivity.

For example, non-metals and metals can be co-doped into the lattice of the photocatalyst in order to accomplish highefficiency selectivity.¹¹⁹ The C and N co-doped TiO₂ nanotubes with Na⁺ ions intercalated between the titanate layers were

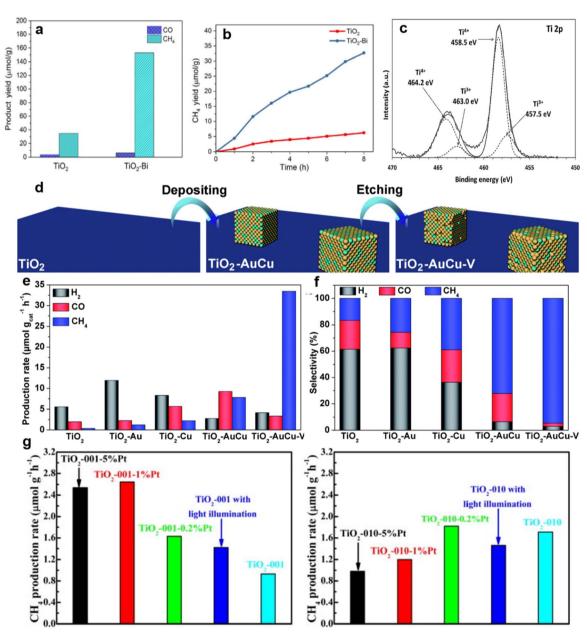


Fig. 7 (a) Product yields of TiO_2 and TiO_2 –Bi after photocatalytic CO_2 reduction for 14 h. (b) Photocatalytic CH_4 generation of TiO_2 and TiO_2 –Bi. Reproduced with permission from ref. 122. Copyright 2018 Springer. (c) A high-resolution XPS spectrum of Ti 2p of 10% I– TiO_2 . Reproduced with permission from ref. 124. Copyright 2011 Elsevier. (d) The crafting process of TiO_2 –AuCu–V. (e) Yields and (f) selectivity of CH_4 , CO, CH_2 over CH_4 over CH_4

prepared by an alkaline hydrothermal method and achieved an increase in CH₄ yield. 120 Na⁺ ions introduced on the surface of C-N co-doped TiO₂ nanotubes during the synthesis process were proposed to act as the active sites for effective CO₂ absorption and further increase the conversion of CO2 to CH₄.¹²⁰ Similarly, compared with pure TiO₂, V and N co-doped TiO2 nanocube arrays exhibited nearly four times improvement of photocatalytic CO₂ to CH₄ conversion. ¹²¹ In addition to the ions just mentioned, Bi3+ ions adsorbed on the surface of TiO2 nanosheets favoured highly selective CH4 photocatalytic production via stimulating the reduction of intermediate CO.122 In this study, isolated Bi³⁺ ions were confined on the surface of 2D TiO₂ (TiO₂-Bi). 122 Compared with the pure TiO₂ counterpart, the TiO_2 -Bi exhibited a higher photocatalytic selectivity and efficiency of CH₄ (Fig. 7a and b). 122 The mechanism was the consecutive transfer of protons and electrons to intermediate CO, finally producing CH₄, where the introduced Bi³⁺ was

responsible for this fast conversion. 122 Furthermore, halogen element (i.e., Cl, Br and I) doping can improve the catalytic selectivity.123 XPS analysis of I-doped TiO2 revealed that I5+ substituted for Ti⁴⁺ in the lattice (Fig. 7c). 124 As a result, Ti³⁺ was generated to balance the charge (Fig. 7c).124 The high CO selectivity of I-TiO2 was achieved after the I5+ doping. 124 We speculate that the low-valent titanium metal ions here are very likely to be used as active sites to promote the selective occurrence of the reaction, but direct experimental verification is needed.

Liu et al. loaded the Au-Cu alloy on TiO₂ nanosheets (TiO₂-AuCu) by ultrasonic and hydrothermal treatment and then obtained photocatalysts with Cu vacancies (TiO2-AuCu-V) by etching (Fig. 7d).125 In comparison with TiO2, TiO2-Au, TiO2-Cu and TiO₂-AuCu, the CH₄ generation selectivity of TiO₂-AuCu-V was dramatically elevated to 94.7% (Fig. 7e and f).125 The removal of Cu atoms at the surface of TiO2-AuCu-V enhanced

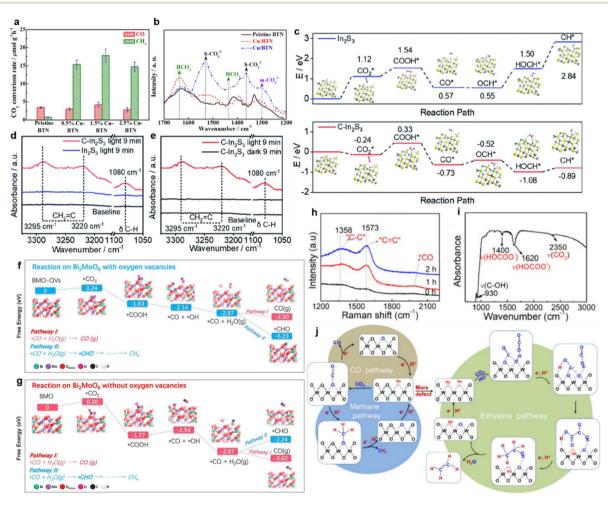


Fig. 8 (a) CO₂ photoreduction rate over pristine BTN and Cu-BTN with different amounts of Cu decoration. (b) In situ DRIFTS IR spectra of pristine BTN, Cu-BTN and Cu/BTN (obtained by depositing Cu on the as-prepared brookite TiO2 nanocubes). Reproduced with permission from ref. 61 copyright 2017 Wiley. (c) Calculated reaction energy diagrams of CO₂ to CH* over the H-terminated surfaces of pristine In_2S_3 and C- In_2S_3 . In situ DRIFTS spectra of (d) In₂S₃ and (e) C-In₂S₃. Reproduced with permission from ref. 133 copyright 2020 Royal Society of Chemistry. Reaction pathways of CO₂ reduction over BiMoO₆ (f) with oxygen vacancies and (g) without oxygen vacancies. Reproduced with permission from ref. 63 copyright 2019 Elsevier. (h) Raman spectra of WO_{3-x} during the photocatalytic CO_2 reduction. (i) IR spectrum of WO_{3-x} after photocatalysis. (j) Schematic diagram of possible pathways of C₂H₄, CH₄ and CO generation via photocatalytic CO₂ reduction over WO_{3-x}. Reproduced with permission from ref. 62 copyright 2020 Elsevier.

the electron trapping ability, consequently providing sufficient electrons for the generation of $\mathrm{CH_4}$ as mentioned above. Moreover, the experimental results also showed that there is a strong correlation between the yield of $\mathrm{CH_4}$ and the low-coordination Cu atoms near the vacancies, indicating that these Cu atoms could be used as active sites for the conversion of $\mathrm{CO_2}$ to $\mathrm{CH_4}$, further enhancing the selectivity of $\mathrm{CH_4}$ generation. 125

Interestingly, although some metals have been proven to be able to improve selectivity in research, the same kind of metal loaded on different crystal faces of a special catalyst may exhibit different site activities. Taking the commonly used anatase TiO2 catalyst as an example, the theoretical surface energy order of the low index facets is $\{101\}$ (i.e., 0.44 J m⁻²) $< \{010\}$ (i.e., 0.53 J m^{-2}) < {001} (i.e., 0.90 J m⁻²). This means that the most stable {101} facets exhibit the lowest catalytic reactivity for the CO₂ reduction. Thus, in order to manipulate products and achieve high photocatalytic efficiency, ratios of {001} to {010} TiO₂ exposed facets were tuned. ¹²⁸ Due to the strong interaction between CO₂ and the {010} surface of TiO₂, anatase TiO₂ rods with dominant {010} facets accomplished the efficient photoreduction of CO2 to CH4.128 Ma reported that after Pt loading, anatase TiO2 exposing {001} facets exhibited improved CH4 evolution rates.129 After modifying Pt on {001}TiO2 facets, uniform Pt nanoparticles acted as active sites and led to a higher CH₄ yield. However, when decorated on the {010} TiO₂ facets, Pt nanoparticles agglomerated, exerting a negative effect on the photocatalytic reaction (Fig. 7g). 130

To sum up, the introduction of metals, vacancies, and different ions to the photocatalysts might serve as active sites for the selective conversion of CO_2 to the target products. However, the relationship between the active sites and the high reaction selectivity is not clear. The roles of some special ions, such as low-valence metal ions (Ti^{3+}) generated together with the Vo (Fig. 7c) during the selective CO_2 reduction reaction have not been fully assessed. Many of the discussions about the active sites just put forward conjectures that need to be further investigated by experiment.

3.2. Intermediates

3.2.1. Formation energy of crucial intermediates. To produce high-value-added products, the formation of some key intermediates is particularly significant.^{131,132} Taking the selective formation of CH₄ as an example. There are two reaction paths after the formation of *CO. One is that *CO is released from the surface to generate CO, and the other is that *CO is hydrogenated to generate *CHO and finally converted to CH₄. It can be seen that the formation energy of *CHO is lower than that of *CO, and the reaction is inclined to generate CH₄. The formation energy of intermediates could be reduced *via* metal loading, vacancy construction and ion modification.

Cu-nanocluster-decorated brookite TiO₂ quasi-nanocubes (Cu-BTN) exhibited good activity and selectivity (Fig. 8a).⁶¹ When using 1.5% Cu-BTN as photocatalysts, the main products were CH₄, accounting for about 85% of the total amount of final products.⁶¹ The reason for this high photocatalytic selectivity of

Cu-BTN was explained as follows. When ${\rm CO_3}^{2-}$ ions were intermediates, CO would be the main product, while more ${\rm CH_4}$ would be produced if ${\rm HCO_3}^-$ ions were intermediates. With the introduction of Cu nanoclusters and the gradual increase within the appropriate range, the formation of ${\rm HCO_3}^-$ on the surface of Cu-BTN would become easier (Fig. 8b); finally, ${\rm CH_4}$ would be formed selectively. 61

In addition to the experimental characterization of the formation of key intermediates, the free energy of intermediate formation was studied through theoretical calculations. Wang achieved a $\rm C_2H_4$ production selectivity close to 50% over C-doped $\rm In_2S_3$ nanosheets. 133 According to the calculated reaction energy, the reaction Gibbs free energies from OCH* to HOCH* and from HOCH* to CH* on C-In_2S_3 were -0.56 and 0.19 eV, respectively, which were much lower than the corresponding energies on pure $\rm In_2S_3$ (i.e., 0.95 and 1.34 eV), respectively (Fig. 8c). 133 It was indicated that OCH* could be further hydrogenated to form CH* on C-In_2S_3 (Fig. 8d and e). 133 Meanwhile, unsaturated *CH_2=C, one of the important intermediates to produce $\rm C_2H_4$, could be observed on the surface of C-In_2S_3 in the *in situ* DRIFTS spectra, which was not detected on pure $\rm In_2S_3$ (Fig. 8d and e). 133

Similarly, Yang et al. prepared Bi₂MoO₆ nanosheets containing oxygen vacancies via a facile one-step solvothermal process.63 According to the calculated stepwise Gibbs free energy (Fig. 8f and g), the further hydrogenation of the intermediate CO* to the *CHO over Bi₂MoO₆ with oxygen vacancies was thermodynamically supported, compared to Bi₂MoO₆ without oxygen vacancies. 63 Since *CHO was the prerequisite for the synthesis of CH₄, it could be accompanied by the subsequent hydrogenation steps, ultimately realizing the highly selective CH₄ production of 96.7% under visible light irradiation.63 The tuning of the energy barrier by oxygen vacancies was further confirmed on the surface of Ni-TiO2.136 Besides the theoretical calculations, the important intermediate formation could be identified by experiments.62 For instance, the photocatalytic selectivity of WO3-x micro-rods reducing CO2 to C2H4 increased to 89.3% after introducing oxygen vacancies.62 It could be observed in Raman and Infrared (IR) spectra that essential intermediates, including C=C, C-C, adsorbed CO and HOCOO, appeared (Fig. 8h and i). It was indicated that adjacent oxygen vacancies provided active sites for C-C coupling to generate C_2H_4 . The CO_2 reduction pathway on the WO_{3-x} was proposed to be $CO_2 \rightarrow \cdot COOH \rightarrow (COOH)_2 \rightarrow CH_3COOH \rightarrow$ CH₃CH₂OH → CH₂CH₂ via a hydrogenation and dehydration process (Fig. 8j).62 Apart from the reactions mentioned above, CO2 could also be selectively reduced to methanol, formic acid and other hydrocarbons.74,75,137 For example, the energy barrier of the rate-limiting step ($CO_2 \rightarrow HCOO$) on the surface of MXene (0.53 eV) for the reduction of CO₂ to HCOOH is much lower than that of anatase (0.87 eV), which was prone to producing HCCOH.97

Besides, metal vacancies of semiconductors can adjust the formation energy of intermediates, thereby affecting the photocatalytic reaction.¹³⁴ Since ZnS samples possessing Zn vacancies could be obtained by acid etching over commercial ZnS powders, different pH values of sulfuric acid were used to craft

ZnS containing various amounts of Zn vacancies and obtained different HCOOH formation selectivities (Fig. 9a and b). 134 Acidetched ZnS attained the highest selectivity of 86.6% for HCOOH production at pH = $0.2.^{134}$ As displayed in Fig. 9c, with the existence of Zn vacancies, ZnS required a lower energy barrier for the reduction of CO₂ to HCOOH.¹³⁴ Moreover, hydroxyl groups on the surface might bind closely with CO₂ molecules to form key intermediates during the photocatalytic CO₂

reduction. 135 The proposed CH4 formation mechanism on the hydroxylated mesoporous TiO₂ surface is shown in Fig. 10d. 135 According to the experimental results, on the hydroxylabundant surface of TiO2, the -OH groups could convert absorbed CO2 molecules to carbonate or bicarbonate species (Fig. 9d). 135 The bidentate carbonate (b-CO₃²⁻) species sequentially received 2 electrons and 2 protons and were transformed into CH₄ through the sequence of Ti-OOCH₂ → Ti-O-CH₃ →

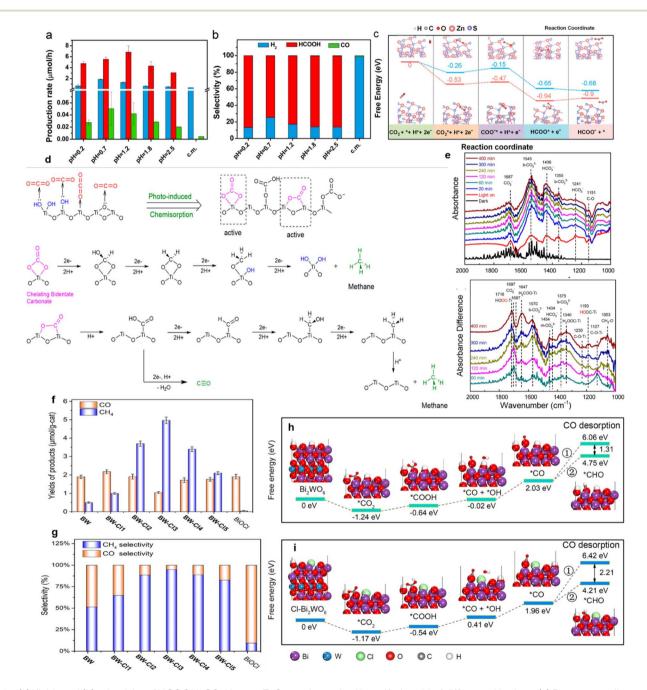


Fig. 9 (a) Yields and (b) selectivity of HCOOH, CO, H2 over ZnS samples etched by sulfuric acid of different pH values. (c) Free energy diagram for the pathways of CO₂ conversion to formate on a perfect ZnS (blue) and V_{Zn}-ZnS (pink) surface. Reproduced with permission from ref. 134 copyright 2019 American Chemical Society. (d) Proposed CH₄ and CO formation mechanism on the hydroxylated surface of TiO₂. (e) The DRIFT spectra of adsorbed and transformed species on the hydroxylated surface of TiO2 after different light irradiation times. Reproduced with permission from ref. 135 copyright 2020 American Chemical Society. (f) Yields and (g) selectivity of CO and CH₄ over BW, BiOCl, and BW-Cl_x (x = 1) 1-5) after photocatalytic CO₂ reduction for 3 h. Free energy diagrams of CO₂ photoreduction over (h) Bi₂WO₆ and (i) Cl⁻-modified Bi₂WO₆. Reproduced with permission from ref. 70 copyright 2020 American Chemical Society.

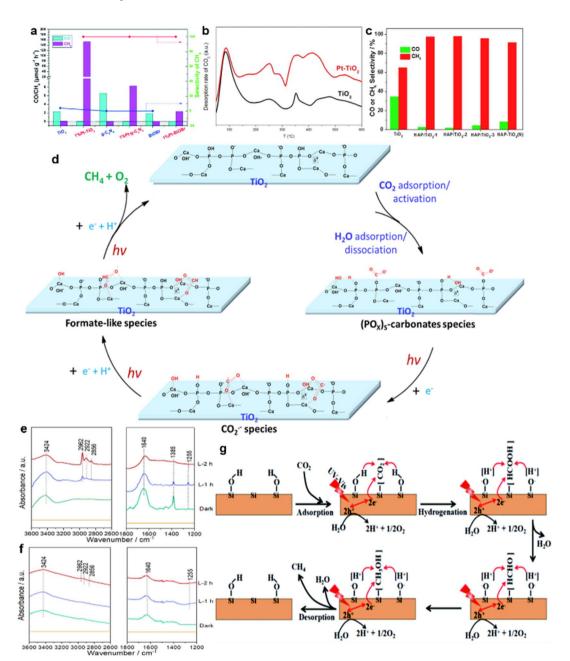


Fig. 10 (a) Photocatalytic activities and selectivities of CO_2 reduction over TiO_2 , $g-C_3N_4$ and BiOBr with or without Pt loading. (b) CO-TPD of TiO_2 and $Pt-TiO_2$. Reproduced with permission from ref. 58 copyright 2018 Royal Society of Chemistry. (c) The evolution rates and the selectivity of CO and CH_4 over TiO_2 and various HAP/ TiO_2 photocatalysts. (d) A possible pathway for the conversion of CO_2 to CH_4 over $Pt/HAP/TiO_2$ in the presence of $Pt/HAP/TiO_2$ and (f) Pt/TiO_2 . Reproduced with permission from ref. 68 copyright 2018 Elsevier. (g) Schematic illustration of the photocatalytic CO_2 conversion to CH_4 over hydroxylated SiC nanosheets. Reproduced with permission from ref. 141 copyright 2019 Royal Society of Chemistry.

CH₄ (Fig. 9d).¹³⁵ Meanwhile, the carboxylic species experienced the process of Ti–COOH \rightarrow Ti–CHO \rightarrow Ti–CH₂OH \rightarrow Ti–CH₃ \rightarrow CH₄ to produce CH₄ (Fig. 9e).¹³⁵

Ion modification can also improve the selectivity of $\rm CO_2$ reduction by adjusting the formation energy of key intermediates. Li prepared $\rm Bi_2WO_6$ (BW) nanosheets loaded with different amounts of $\rm Cl^-$ ions, which were marked as $\rm BW-Cl_x$ (x=1-5). A maximum selectivity of 94.98% for $\rm CH_4$ generation was achieved on the surface of $\rm BW-Cl_3$ (Fig. 9f and g). In the

presence of Cl $^-$ ions, the half-reaction (*i.e.*, oxygen evolution) of Bi $_2$ WO $_6$ nanosheets was greatly increased. To Simultaneously, the produced protons facilitated the formation of CH $_4$. Moreover, DFT calculations (Fig. 9h and i) confirmed that the presence of Cl $^-$ ions on Bi $_2$ WO $_6$ nanosheets was capable of lowering the energy barrier for the generation of crucial intermediate (*i.e.*, *CHO), thus enhancing CH $_4$ production.

In the above reports, the existence of key intermediates in some highly selective systems was verified by the experimental data, and the formation energy of the target intermediates was studied through theoretical calculations. The difficulty in producing intermediates and the stability of the as-obtained intermediates will be discussed in the next section.

3.2.2. Stability of intermediates. In order to synthesize high-value-added products, the stability of target intermediates should be taken into account.139 Stable intermediates facilitate electron transfer reactions in the subsequent hydrogenation process, while instability would lead to rapid desorption from the surface of photocatalysts and the reaction ends at this step. As mentioned in the previous section, the intermediate *CHO is crucial for the formation of CH₄, and it should be guaranteed that not only the formation energy of *CHO is low, but also *CHO is stable enough to generate CH₄. The high stability of key intermediates could be achieved through the loading of precious metals and the combination of different materials.

For instance, the introduction of noble metals could reduce the intermediate desorption capacity of the photocatalysts and ensure that the intermediates are adsorbed on the surface of the catalysts for subsequent reactions.⁵⁸ As shown in Fig. 10a, compared with pure semiconductor photocatalysts, nearly 100% selectivity of CH₄ generation was achieved by loading 1% Pt on the TiO2, C3N4 and BiOBr photocatalysts, respectively. 56,58,140 The temperature-programmed desorption (TPD) results confirmed that CO demonstrated an especially strong adsorption capacity on the Pt clusters (Fig. 10b).58 Meanwhile, since only physical adsorption occurred between CH₄ and the Pt clusters, CH₄ exhibited low adsorption energy on the Pt clusters, leading to the easy desorption of generated CH4 from the Pt surface.58 Thus, most CO products produced during the photocatalytic process were anchored on the catalyst surfaces, and CH₄ molecules were desorbed from the photocatalyst surface, eventually achieving enhanced selectivity of CH₄ generation.⁵⁸

Through compound modification of the catalysts, the stability of some key intermediates can also be improved. Hydroxyapatite (HAP)-decorated TiO2 could achieve 99.1% selectivity of CH₄ generation (Fig. 10c).⁶⁸ The formation of much more stable intermediates over HAP/TiO2 nanorods was responsible for this selectivity enhancement.⁶⁸ A possible pathway for the conversion of CO2 to CH4 over Pt/HAP/TiO2 in the presence of H₂O is proposed in Fig. 10d.⁶⁸ Specifically, the formate-like species (HCOO-) was identified as the crucial intermediate for CH₄ production.⁶⁸ Compared with that of TiO₂, IR peaks at 3000-2800 cm⁻¹ of Pt/HAP/TiO₂ were obviously enhanced, indicating that the HAP effectively improved the stability of HCOO (Fig. 10e and f).68

Besides, as the cocatalyst of P25, surface alkalization of Ti₃C₂ could dramatically enhance the evolution rate of CH₄ (16.61 μmol g⁻¹ h⁻¹),¹⁴² in which surface hydroxyls on selective CH₄ generation over SiC nanosheets have gained much attention.141,143 Hydroxyl groups on the surface of SiC nanosheets boosted the photoreduction of CO_2 into CH_4 , achieving the CH_4 generation selectivity of about 80%.141 The mechanism is depicted in Fig. 10g. 141 Specifically, -OH groups on the surface of SiC could provide sufficient protons to CO₂, which is critical to the CO2 activation.141 Moreover, the intermediates could be stabilized by forming hydrogen bonds between the

intermediates and -OH groups. These effects improved the selective CH₄ generation.¹⁴¹

Although the stability of the intermediates remarkably affects the reaction path of photocatalytic CO₂ reduction, the relative investigations are limited in scope. More attention should be paid to the generation process and stabilization of key intermediates to make the study on CO2 reduction more comprehensive and convincing.

3.3. Desorption of products

As one critical step in the entire CO₂ reduction process, the desorption of the product from the surface of photocatalysts affects the selectivity. The rapid release of the product prevents the subsequent reaction, thereby maintaining the selective and continuous yield of this product. Various types of vacancies and crystal facets cause varied adsorption capabilities of products, which results in the adjustment of the final products.

Metal vacancies of semiconductors play a significant role in manipulating the photocatalytic selectivity. Different reduction products can be obtained by introducing various metal vacancies.144 Selective CO generation could be achieved on the surface of BiOBr ultrathin nanosheets containing abundant Bi vacancies (VBi).144 Compared with BiOBr nanosheets without VBi, CO could be more easily desorbed from the surface of V_{Bi}-BiOBr, leading to increasing the amount of CO production.144

In addition to the introduction of vacancies, some facets of photocatalysts may exhibit the unique ability of CO₂ adsorption and product desorption.145-147 These beneficial effects can enhance the photocatalytic selectivity. As shown in Fig. 11a, distinguished from chemisorbed CO with a larger endothermic

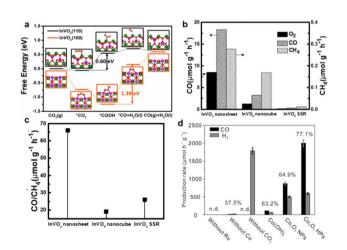


Fig. 11 (a) The photocatalytic activity and (b) the production rates of CO to CH₄ over the ultrathin InVO₄ nanosheets, nanocubes, and obtained by SSR. (c) Calculated Gibbs free energy profiles of photocatalytic CO₂ reduction to CO over InVO₄ of the (110) and (100) planes, respectively. Reproduced with permission from ref. 148 copyright 2019 American Chemical Society. (d) Photocatalytic production rate using β-Co(OH)₂, Co₃O₄ nanoparticles (Co₃O₄ NPs), or Co₃O₄ hexagonal platelets (Co_3O_4 HPs) as catalysts under visible light ($\lambda > 420$ nm) irradiation. Reproduced with permission from ref. 150 copyright 2016 Wiley.

value of 0.45 eV on the {100} facet, the exposed {110} facet of the InVO₄ atomic layer was confirmed to weakly bind the generated CO, leading to the quick desorption of CO molecules from the catalyst surface. Therefore, by the facet engineering technique, ultrathin InVO₄ nanosheets possessing the {110} facet could gain much higher CO formation selectivity (*i.e.*, 98%) as compared with regular InVO₄ nanocubes showing the (100) facet and the bulk InVO₄ obtained by a conventional solid-state reaction (SSR, Fig. 11b and c). Due to the favorable CO₂ absorption and easy desorption of CO, hexagonal Co₃O₄ nanoplatelets exposing {112} facets could realize the selectivity of 77.1% for CO generation (Fig. 11d). Page 110.

In general, both metal vacancies and crystal facets have selective desorption capacity. However, it is unknown whether other modification methods could mediate the desorption ability of products. There is limited discussion in this area, and further exploration is expected.

4. Summary and outlook

There has been widespread interest in the fact that photocatalytic product selectivity is one of the crucial factors limiting the application of photocatalytic CO2 reduction. The importance of photocatalytic CO2 reduction to energy utilization and environmental protection is summarized at the beginning of this review. We introduced different reaction steps that could increase the selectivity of the reaction, that is, the adsorption and activation of reactants (including CO2 adsorption and H2 evolution inhibition, electron supply and others), the formation and stabilization of intermediates (including formation energy of crucial intermediates and stability of intermediates), and the desorption of products. The corresponding modification methods for achieving selective improvement at each stage are summarized, including noble metal decoration, metal and nonmetal doping, vacancy engineering, facet engineering, composite construction, hydroxyl modification and other decoration techniques. Although this research field has been developed for several decades, the photocatalytic conversion of CO2 to high-value products selectively is still in its infancy. A lot of effort should be made to achieve a great breakthrough.

Firstly, although many materials have been successfully fabricated for highly selective photocatalytic CO₂ reduction, the photocatalytic mechanism of high selectivity remains unclear. Most mechanisms have been proposed based on the simulation results instead of experimental data. In addition, plenty of intriguing phenomena, such as the formation of low-valent metal ions near the oxygen vacancies, and the production of surface hydroxyl groups, have been described but no explanations are given in detail. Therefore, more *in situ* characterization techniques, such as FITR, Raman, XRD and NMR, should be conducted to uncover the underlying photocatalytic process. To design highly selective catalysts on purpose, a deep understanding and exploration of the reaction must be gained.

Secondly, more investigations should be focused on the oxidation reaction during photocatalytic CO₂ reduction. Since main products are obtained *via* reducing CO₂, most research is concentrated on the reduction reaction caused by the photo-

generated electrons. However, as a half-reaction of the entire CO₂ reduction, how photo-induced holes participate in the photocatalytic reaction might dramatically affect the catalytic performance of semiconductors. Once the oxidation reaction is restricted, it will be tough for the entire process to proceed. A quick oxidation half-reaction can suppress the inverse reactions of CO₂ reduction. In addition, the oxidation products might participate in the reaction of CO₂ reduction. Therefore, to have a comprehensive understanding of the entire CO₂ reduction process, the oxidation half-reaction involving photo-generated holes requires more in-depth investigations.

Thirdly, precise modification techniques of photocatalysts should be further improved. The introduction of impurities into the lattice of semiconductors can increase the effective capture of electrons and thus improve the selectivity of CH₄ generation. However, there is always an optimal doping concentration. Similarly, the construction of vacancies can bring about an increase in selectivity but excessive vacancies will destroy the bulk structure and reduce the catalytic performance. More delicate methods should be developed to craft decorated photocatalysts.

Fourthly, based on this review, it was found that each step during the entire CO₂ reduction can affect selectivity, so different modification methods could be combined to synergistically boost the reaction selectivity. For example, after oxygen vacancies were introduced into Pt-loaded Ga₂O₃, the selectivity of the reaction increased to nearly 100%. The oxygen vacancies served as the main sites for CO₂ adsorption, while Pt nanoparticles used the hydrogen formed in the photocatalytic decomposition process to reduce the adsorbed CO₂. This synergy increased photocatalytic production selectivity. Besides, the photocatalytic conditions of the catalytic system can influence the production selectivity, including temperature, pressure, gas flow rate, reaction solution, *etc.* Thus, more explorations can be concentrated on adjusting the composition of photocatalysts and the reaction parameters.

In summary, photocatalytic CO₂ conversion to fuel products can not only alleviate carbon dioxide emissions but also provide clean chemical energy using green solar light. To realize high catalytic efficiency and achieve value-added products of high selectivity, the above four points require numerous efforts to explore. More advanced in situ characterization techniques, including solid-state NMR, isotope research, FITR, Raman, and XRD should be applied to study the chemical evolution of catalysts during the catalytic process. To understand the entire reaction process more comprehensively, more studies should be conducted that pay attention to both the reduction halfreaction and the oxidation half-reaction since how photoinduced electrons and holes participate in the photocatalytic reaction will affect the catalytic performance. Due to the different effects of various modification strategies on the reaction process, the modification process should be controlled more accurately, which requires more advanced synthesis equipment and more delicate fabrication strategies. Different modification techniques could be combined to synergistically achieve higher efficiency and selectivity.

Author contributions

M. W. conceived the idea. M. W., S. Y. designed the conceptualization. S. Y., J. H., F. G., H. W., J. L., Y. B. performed the investigation and data curation. J. F., F. H., F. Z. conducted the supervision. M. W., S. Y. wrote the paper. All authors participated in the review and editing of the paper.

Conflicts of interest

There are no conflicts to declare.

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