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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 CO₂ 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.

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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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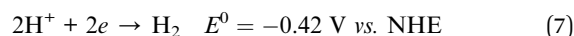
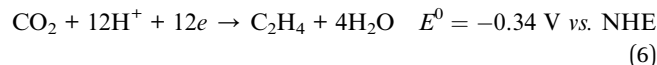
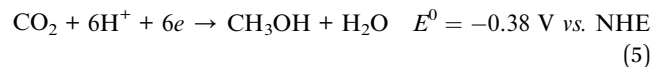
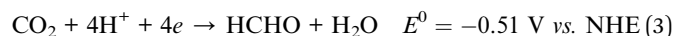


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1. Introduction

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}

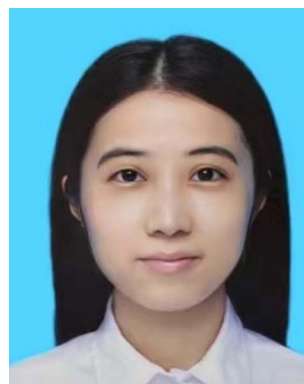


Thus, CO₂ reduction exhibits limited selectivity in aqueous solutions due to the critical challenge of overcoming the competition with the hydrogen evolution reaction (HER). In addition, the reduction potentials of converting CO₂ to different products are similar (eqn (1)–(6)).⁴¹ This phenomenon results in an undesirable mixture of products, which is hard to separate and utilize. Therefore, the improvement in selectivity is of key importance for photocatalytic CO₂ reduction.^{42–45}

This review aims to summarize recent impressive developments in the highly selective photocatalytic CO₂ reduction. After a brief discussion that motivates the research on high product selectivity, the reaction mechanism of photocatalytic CO₂ 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.*, CO₂ 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.

2. 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 photo-generated 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

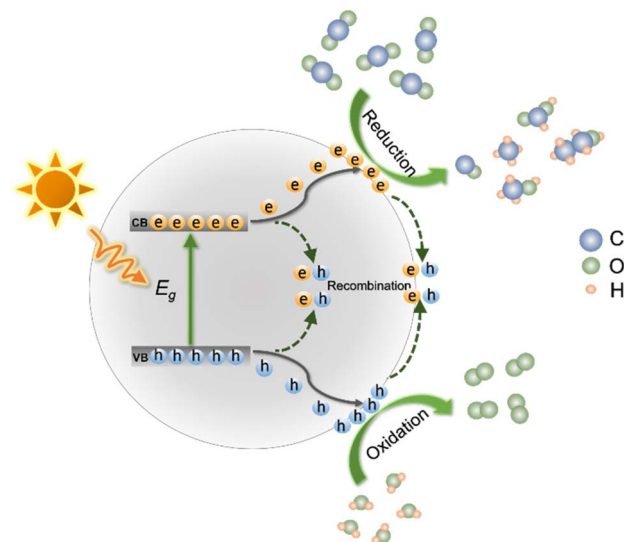
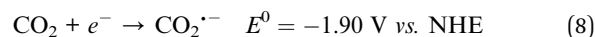


Fig. 2 Schematic illustration of photocatalytic CO₂ reduction.

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



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 (V_O-rich) 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.⁸⁴ Besides, in the noble-metal-free 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.⁸⁵ This kind of modification changed the hydrophilicity and hydrophobicity of the photocatalyst surface and thus mediated the reaction process.⁸⁵ This improved selectivity was attributed to the efficient CO₂ adsorption, triggering efficient CO₂ photoreduction.⁸⁵

Different crystal faces possess different CO₂ adsorption capacities.⁸⁶ 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.⁸⁷ Therefore, oxygen vacancies were prone to form on the surface of ZnO.⁸⁷ These vacancies could preferentially capture CO₂ molecules and work as reduction sites for CO₂.⁸⁷ As a consequence, the CO molecules could be produced as the main products.⁸⁷ In addition, BiOBr nanosheets exposing {001} facets were successfully synthesized in the presence of nitric acid.⁸³ Compared to the BiOBr nanosheets prepared in the absence of nitric acid (BiOBr-0), the {001} facets-dominated BiOBr nanosheets exhibited more efficient CO₂ adsorption and activation, selectively converting CO₂ to CO (Fig. 3c).⁸³

The adsorption and activation capacity can also be improved by changing the structure of the material. Typically, g-C₃N₄-based composite catalysts display strong CO₂ capture ability, which promotes the generation of CO rather than H₂.⁸⁸

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

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
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 μL H ₂ O	CH ₄ (25.69 μmol g ⁻¹ h ⁻¹), 99%	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 ₂ SO 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 ₂ H ₄ (61.6 μmol g ⁻¹ h ⁻¹), 89.3%	62
BiMoO ₆	300 W Xe lamp	50 mg of catalysts, 1.50 g NaHCO ₃ and 5 mL H ₂ SO 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 ₂ O	CO (7 μmol g ⁻¹ h ⁻¹), nearly 100%	64
g-C ₃ N ₄ /FeWO ₄	Visible light (λ > 420 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 ₃ N ₄ /Pd ₉ Cu ₁ H _x	Visible light	15 mg of catalysts, CO ₂ and H ₂ O	CH ₄ (1.20 μmol g ⁻¹ h ⁻¹), nearly 100%	69
Cl ⁻ /Bi ₂ 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 μmol 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 ₂ O	Hydrocarbon fuels (CH ₄ , C ₂ H ₄ , and C ₂ H ₆) (25.06 μmol g ⁻¹ h ⁻¹), 85%	73
V-defective BiVO ₄	300 W Xe lamp	100 mg of catalysts, CO ₂ and H ₂ O	CH ₃ OH (398.3 μmol 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 μmol 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 ₂ O	CH ₄ and C ₂ H ₄ (11.91 μmol 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 μmol 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), 99.6%	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

CO₂ reduction reaction can be significantly improved. Therefore, the target reaction occurs instead of the competitive hydrogen evolution. However, in previous reports about the first

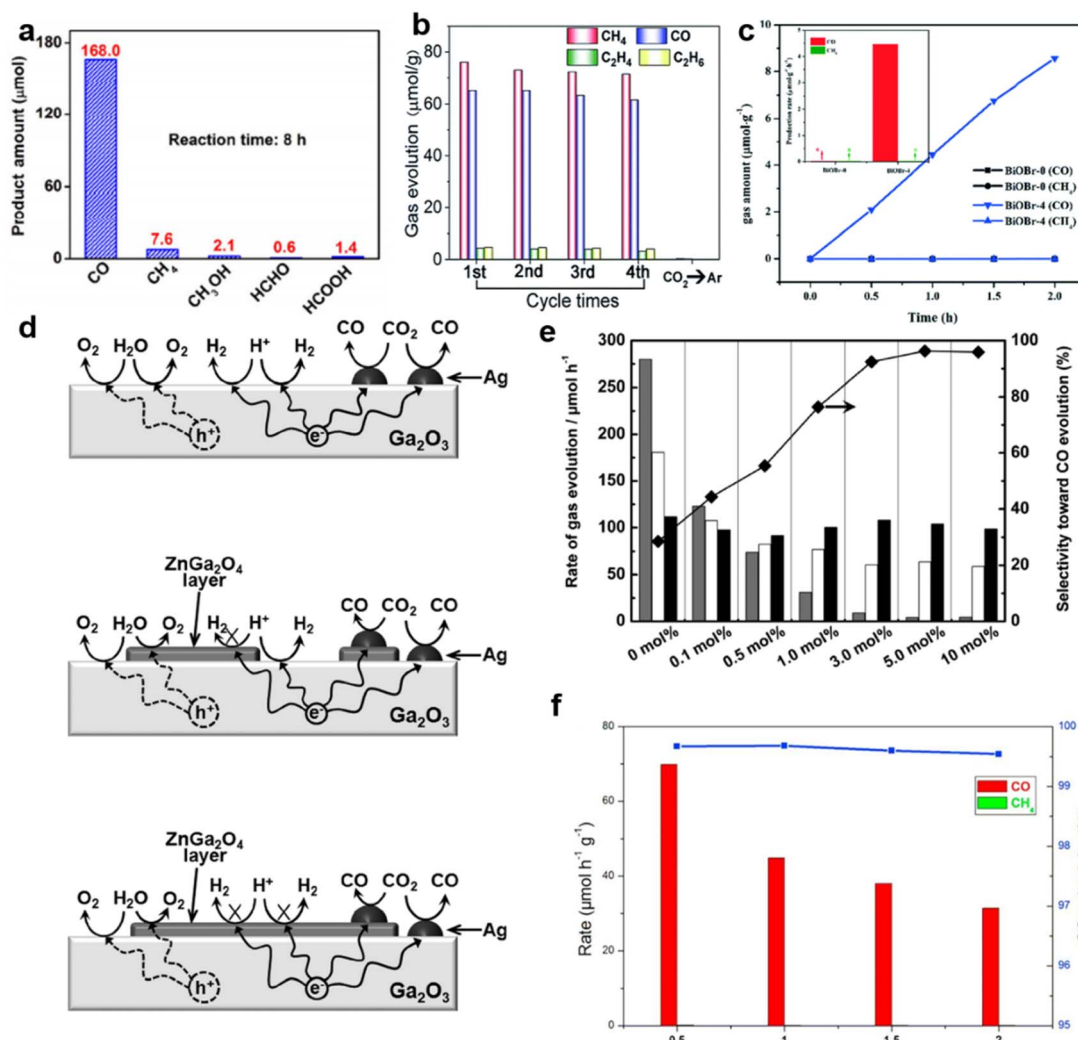


Fig. 3 (a) The amount of products over V_{O-} -enriched Pt– Ga_2O_3 after irradiation for 8 h. Reproduced with permission from ref. 81 copyright 2018 Springer. (b) Photocatalytic yield and stability of Au–Pd-alloy-decorated TiO_2 . Reproduced with permission from ref. 73. copyright 2019 Royal Society of Chemistry. (c) Production rates of CH_4 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 CO_2 in H_2O over Ag-loaded Ga_2O_3 , Ag-loaded Zn-modified Ga_2O_3 with a low Zn content, and Ag-loaded Zn-modified Ga_2O_3 with a high Zn content. (e) Evolution rates of CO (black), O_2 (white), and H_2 (gray) in the photocatalytic conversion of CO_2 over Ag-loaded $ZnGa_2O_4$ -modified Ga_2O_3 containing different amounts of $ZnGa_2O_4$. 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 CO_2 reduction reaction, there is a lack of the selective generation of different carbon reduction products. In addition, how CO_2 adsorption mediates carbon products needs to be further explored.

3.1.2. Electron supply. The formation of high-value-added products such as CH_4 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, $LaPO_4$ reached a 5.6 times enhancement in CH_4 yield compared to pure $LaPO_4$ (Fig. 4a).⁵³ The selectivity of CH_4 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 eight-electron reduction of CO_2 to CH_4 .⁵³ This mechanism was proved in another report, where Pt/ Cu_2O nanoparticles trapped sufficient photogenerated electrons and ensured the multielectron photocatalytic reactions to form CH_4 (Fig. 4b–d).⁹⁷ It is noteworthy that the electron sink effect of Pt also exists in other catalysts. The selectivity of CH_4 formation was improved when Pt@Ag core@shell structures were decorated on TiO_2

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/CuO_x-C CNFs demonstrated the highest CH₄ generation rate of 241.6 μmol h⁻¹ g⁻¹ with the selectivity of

~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 yield.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@Ag_{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 $\text{Bi}_6\text{Mo}_2\text{O}_{15}$ sub-microwires with abundant oxygen vacancies, which could capture sufficient photo-generated electrons, are favorable for the photocatalytic reduction of CO_2 to 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 CO_2 molecules.¹⁰² Finally, the CH_4 selectivity was increased from 8.92% to 62.66%.¹⁰²

$\text{g-C}_3\text{N}_4$ -based semiconductor composites could also selectively obtain CH_4 or other fuels.^{112,113} Truc reported that compared with pure $\text{Cu}_2\text{V}_2\text{O}_7$ (*i.e.*, 0) and $\text{g-C}_3\text{N}_4$ (*i.e.*, 0), the

$50\text{Cu}_2\text{V}_2\text{O}_7/50\text{g-C}_3\text{N}_4$ photocatalysts possessed more active electrons in the CB of the $\text{g-C}_3\text{N}_4$.¹¹⁴ Enough electron supply of $50\text{Cu}_2\text{V}_2\text{O}_7/50\text{g-C}_3\text{N}_4$ accomplished the selective generation of CH_4 (*i.e.*, $1696 \text{ mmol g}^{-1} \text{ cat. h}^{-1}$).¹¹⁴ Additionally, in the $\text{g-C}_3\text{N}_4/\text{ZnO}$ system, the electrons of ZnO recombined with the photo-generated holes of $\text{g-C}_3\text{N}_4$, thereby retaining the electrons with strong reduction capability in $\text{g-C}_3\text{N}_4$.¹¹⁵ Sufficient electrons in the CB of $\text{g-C}_3\text{N}_4$ boosted the conversion of CO_2 to CH_3OH .¹¹⁵ ZnO nanorod arrays@carbon fiber (ZnO NA@CF) composites showed highly selective CH_3OH production during the photocatalytic CO_2 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 O_2 and H^+ , while CO_2 molecules were

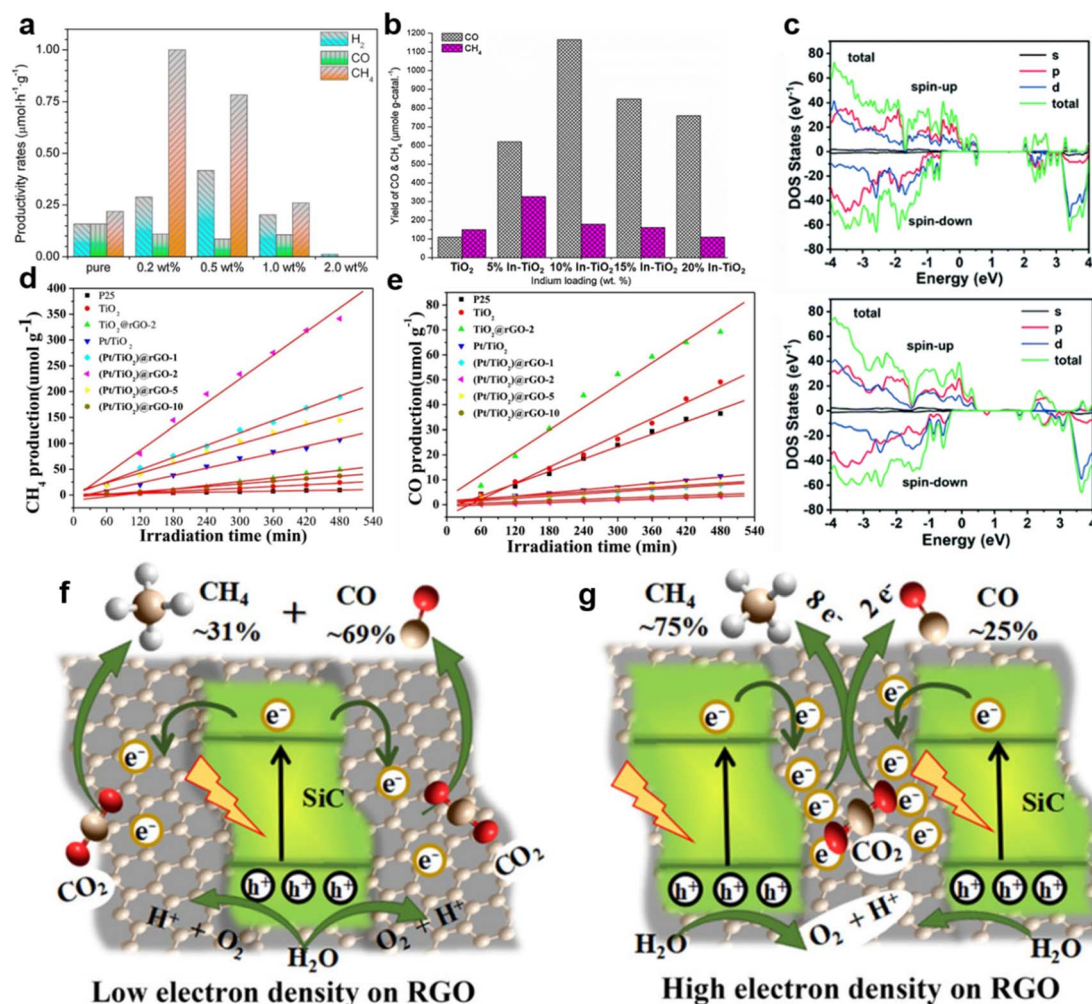


Fig. 5 (a) The production rates of pure TiO_2 and Mg- TiO_2 containing different amounts of Mg doping, reproduced with permission from ref. 100 copyright 2014 Elsevier. (b) The yield of products of In- TiO_2 with different amounts of In doping, reproduced with permission from ref. 101 copyright 2013 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 , $\text{TiO}_2/\text{rGO-2}$ and $(\text{Pt/TiO}_2)/\text{rGO-n}$ 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 CH_3OH by sufficient electrons on the carbon fiber.¹¹⁶ rGO is another appealing photocatalyst that can accumulate electrons of high energy to accelerate CH_4 generation *via* an eight-electron catalytic process.¹¹⁷ Bare rGO is not active for the photocatalytic conversion of CO_2 to CH_4 (ref. 56) but rGO-wrapped Pt/ TiO_2 ($(\text{Pt}/\text{TiO}_2)@\text{rGO}$) photocatalysts achieved excellent selectivity (*i.e.*, 99.1%) of CH_4 evolution (Fig. 5d and e).⁵⁶ Pt nanoparticles in $(\text{Pt}/\text{TiO}_2)@\text{rGO}-n$ photocatalysts functioned as an accumulator for electron transfer in the TiO_2 -Pt-rGO ternary system.⁵⁶ Due to the strong electron-withdrawing capacity of the rGO shell, the photogenerated electrons could further transfer from Pt to rGO.⁵⁶ Thus, the photo-generated electrons were transferred from TiO_2 to Pt and finally to the rGO shell (*i.e.*, $\text{TiO}_2 \rightarrow \text{Pt} \rightarrow \text{rGO}$).⁵⁶ The photo-generated electrons accumulated on the rGO shell and subsequently reacted with the adsorbed CO_2 to produce CH_4 .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 CO_2 reduction, resulting in a high CH_4 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 CH_4 (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 In_2O_3 -2wt% rGO nanocomposite (*i.e.* CH_4 generation rate of $953.72 \mu\text{mol h}^{-1} \text{g}^{-1}$ 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 ($\text{Pt}@h\text{-BN}$) 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 ($\text{Pt}@i\text{-S-AB}$, middle part of Fig. 6d), $\text{Pt}@h\text{-BN}$ with the Pt:B molar ratio of 1:3 ($\text{Pt}@h\text{-BN}_3$) demonstrated the best photocatalytic activity and achieved a nearly 100% selectivity of CO_2 -to- CH_4 (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)

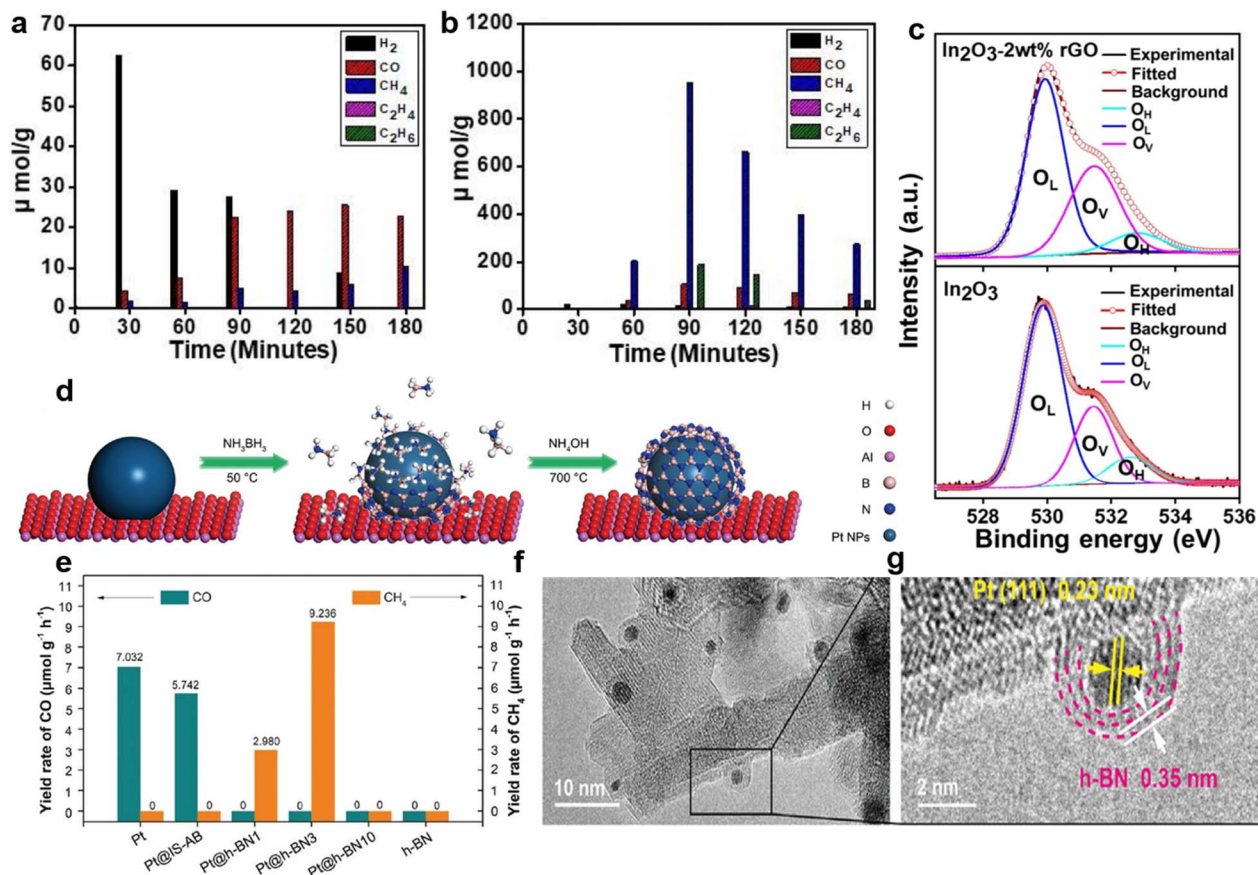


Fig. 6 Generation efficiency of various products over (a) In_2O_3 and (b) In_2O_3 -2 wt% rGO. (c) High-resolution XPS spectra of O 1s of In_2O_3 -2 wt% rGO nanocomposites (upper) and In_2O_3 nanostructures (lower). Reproduced with permission from ref. 109 copyright 2021 Elsevier. (d) Schematic diagram of the synthesis process of $\text{Pt}@i\text{S-AB}$ and $\text{Pt}@h\text{-BN}$ series catalysts originating from Pt. (e) The photocatalytic CO_2 conversion rate of Pt, $\text{Pt}@i\text{S-AB}$, $\text{Pt}@h\text{-BN}$ series catalysts and pure h-BN. (f and g) HRTEM images of $\text{Pt}@h\text{-BN}_3$. Reproduced with permission from ref. 110 copyright 2021 Wiley.

accelerated the electron mobility to produce the key intermediate CO^{2-} species on the surface of $\text{Pt}@h\text{-BN}$.¹¹⁰ Compared to pure BiVO_4 , the lamellar BiVO_4 showed the selective generation of CH_3OH due to efficient electron capture to form $\text{CO}_2^{\cdot-}$ 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 CO_2 to 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 CO_2 to specific products. Appropriate CO_2 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 high-efficiency selectivity.¹¹⁹ The C and N co-doped TiO_2 nanotubes with Na^+ ions intercalated between the titanate layers were

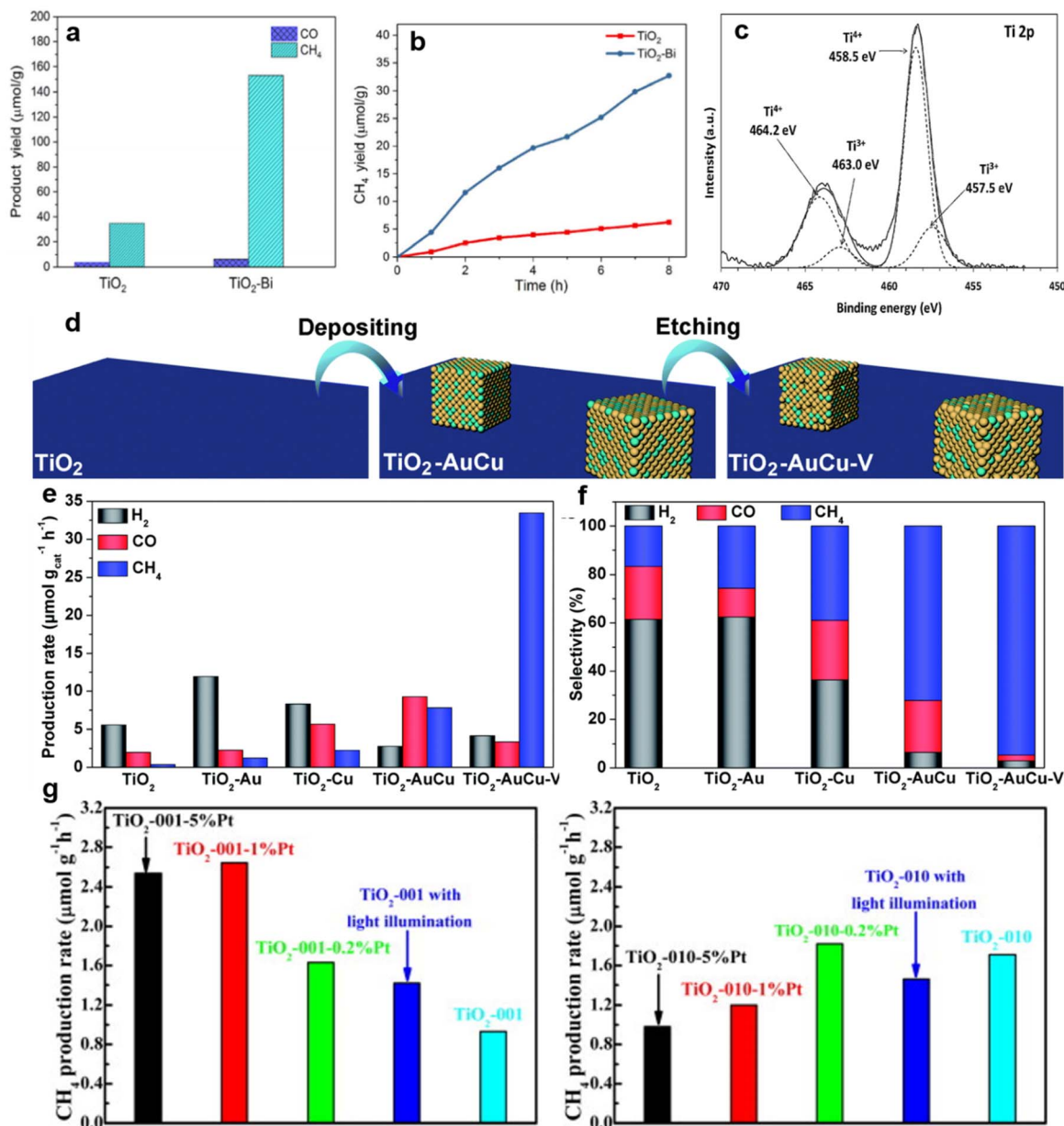


Fig. 7 (a) Product yields of TiO_2 and $\text{TiO}_2\text{-Bi}$ after photocatalytic CO_2 reduction for 14 h. (b) Photocatalytic CH_4 generation of TiO_2 and $\text{TiO}_2\text{-Bi}$. Reproduced with permission from ref. 122. Copyright 2018 Springer. (c) A high-resolution XPS spectrum of Ti 2p of 10% I- TiO_2 . Reproduced with permission from ref. 124. Copyright 2011 Elsevier. (d) The crafting process of $\text{TiO}_2\text{-AuCu-V}$. (e) Yields and (f) selectivity of CH_4 , CO , H_2 over TiO_2 -based photocatalysts. Reproduced with permission from ref. 125 copyright 2019 Royal Society of Chemistry. (g) Photocatalytic reduction activity of CO_2 to CH_4 over $\text{TiO}_2\text{-001}$ and $\text{TiO}_2\text{-010}$ and their corresponding 1 wt% or 5 wt% Pt-loaded products under UV-light irradiation for 4 h. Reproduced with permission from ref. 130 copyright 2014 Elsevier.

prepared by an alkaline hydrothermal method and achieved an increase in CH_4 yield.¹²⁰ Na^+ ions introduced on the surface of C–N co-doped TiO_2 nanotubes during the synthesis process were proposed to act as the active sites for effective CO_2 absorption and further increase the conversion of CO_2 to CH_4 .¹²⁰ Similarly, compared with pure TiO_2 , V and N co-doped TiO_2 nanocube arrays exhibited nearly four times improvement of photocatalytic CO_2 to CH_4 conversion.¹²¹ In addition to the ions just mentioned, Bi^{3+} ions adsorbed on the surface of TiO_2 nanosheets favoured highly selective CH_4 photocatalytic production *via* stimulating the reduction of intermediate CO .¹²² In this study, isolated Bi^{3+} ions were confined on the surface of 2D TiO_2 ($\text{TiO}_2\text{-Bi}$).¹²² Compared with the pure TiO_2 counterpart, the $\text{TiO}_2\text{-Bi}$ exhibited a higher photocatalytic selectivity and efficiency of CH_4 (Fig. 7a and b).¹²² The mechanism was the consecutive transfer of protons and electrons to intermediate CO , finally producing CH_4 , where the introduced Bi^{3+} 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 TiO_2 revealed that I^{5+} substituted for Ti^{4+} in the lattice (Fig. 7c).¹²⁴ As a result, Ti^{3+} was generated to balance the charge (Fig. 7c).¹²⁴ The high CO selectivity of I- TiO_2 was achieved after the I^{5+} 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 TiO_2 nanosheets ($\text{TiO}_2\text{-AuCu}$) by ultrasonic and hydrothermal treatment and then obtained photocatalysts with Cu vacancies ($\text{TiO}_2\text{-AuCu-V}$) by etching (Fig. 7d).¹²⁵ In comparison with TiO_2 , $\text{TiO}_2\text{-Au}$, $\text{TiO}_2\text{-Cu}$ and $\text{TiO}_2\text{-AuCu}$, the CH_4 generation selectivity of $\text{TiO}_2\text{-AuCu-V}$ was dramatically elevated to 94.7% (Fig. 7e and f).¹²⁵ The removal of Cu atoms at the surface of $\text{TiO}_2\text{-AuCu-V}$ enhanced

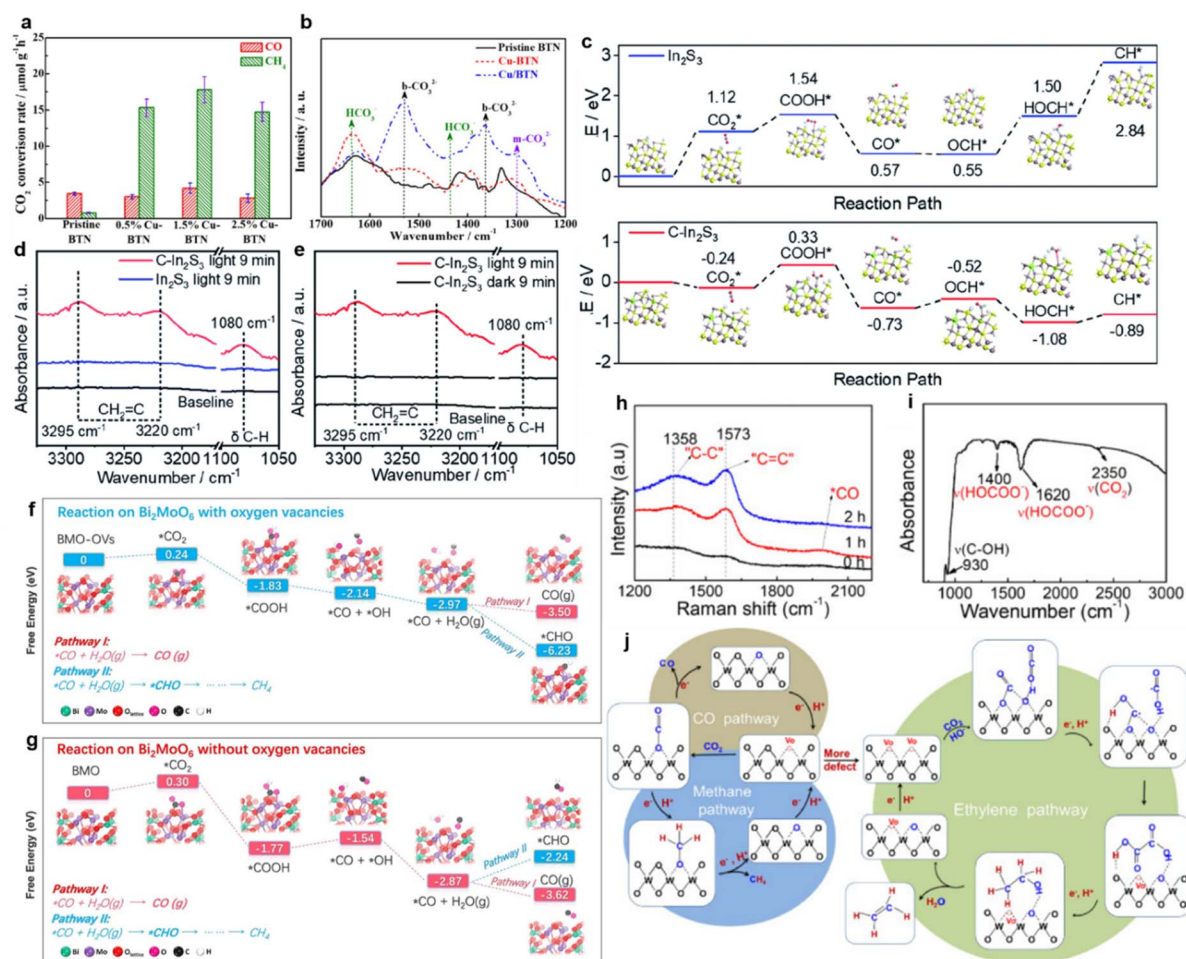


Fig. 8 (a) CO_2 photoreduction rate over pristine BTN and Cu-BTN with different amounts of Cu decoration. (b) *In situ* DRIFTS IR spectra of pristine BTN, Cu-BTN and Cu/BTN (obtained by depositing Cu on the as-prepared brookite TiO_2 nanocubes). Reproduced with permission from ref. 61 copyright 2017 Wiley. (c) Calculated reaction energy diagrams of CO_2 to CH^* over the H-terminated surfaces of pristine In_2S_3 and C- In_2S_3 . *In situ* DRIFTS spectra of (d) In_2S_3 and (e) C- In_2S_3 . Reproduced with permission from ref. 133 copyright 2020 Royal Society of Chemistry. Reaction pathways of CO_2 reduction over BiMoO_6 (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 C_2H_4 , CH_4 and CO generation *via* photocatalytic CO_2 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 CH₄ as mentioned above.¹²⁵ Moreover, the experimental results also showed that there is a strong correlation between the yield of CH₄ and the low-coordination Cu atoms near the vacancies, indicating that these Cu atoms could be used as active sites for the conversion of CO₂ to CH₄, further enhancing the selectivity of CH₄ 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).^{126,127} 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 photo-reduction 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.¹³⁰ 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 CO₂ 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 (Ti³⁺) generated together with the Vo (Fig. 7c) during the selective CO₂ 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 CO₃²⁻ ions were intermediates, CO would be the main product, while more CH₄ would be produced if HCO₃⁻ ions were intermediates.⁶¹ With the introduction of Cu nanoclusters and the gradual increase within the appropriate range, the formation of HCO₃⁻ on the surface of Cu-BTN would become easier (Fig. 8b); finally, CH₄ 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 C₂H₄ production selectivity close to 50% over C-doped In₂S₃ nanosheets.¹³³ According to the calculated reaction energy, the reaction Gibbs free energies from OCH* to HOCH* and from HOCH* to CH* on C-In₂S₃ were -0.56 and 0.19 eV, respectively, which were much lower than the corresponding energies on pure In₂S₃ (*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-In₂S₃ (Fig. 8d and e).¹³³ Meanwhile, unsaturated *CH₂=C, one of the important intermediates to produce C₂H₄, could be observed on the surface of C-In₂S₃ in the *in situ* DRIFTS spectra, which was not detected on pure In₂S₃ (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 WO_{3-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 C₂H₄. The CO₂ reduction pathway on the WO_{3-x} was proposed to be CO₂ → ·COOH → (COOH)₂ → CH₃COOH → 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 (CO₂ → 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 Acid-etched 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 hydroxyl-abundant 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 →

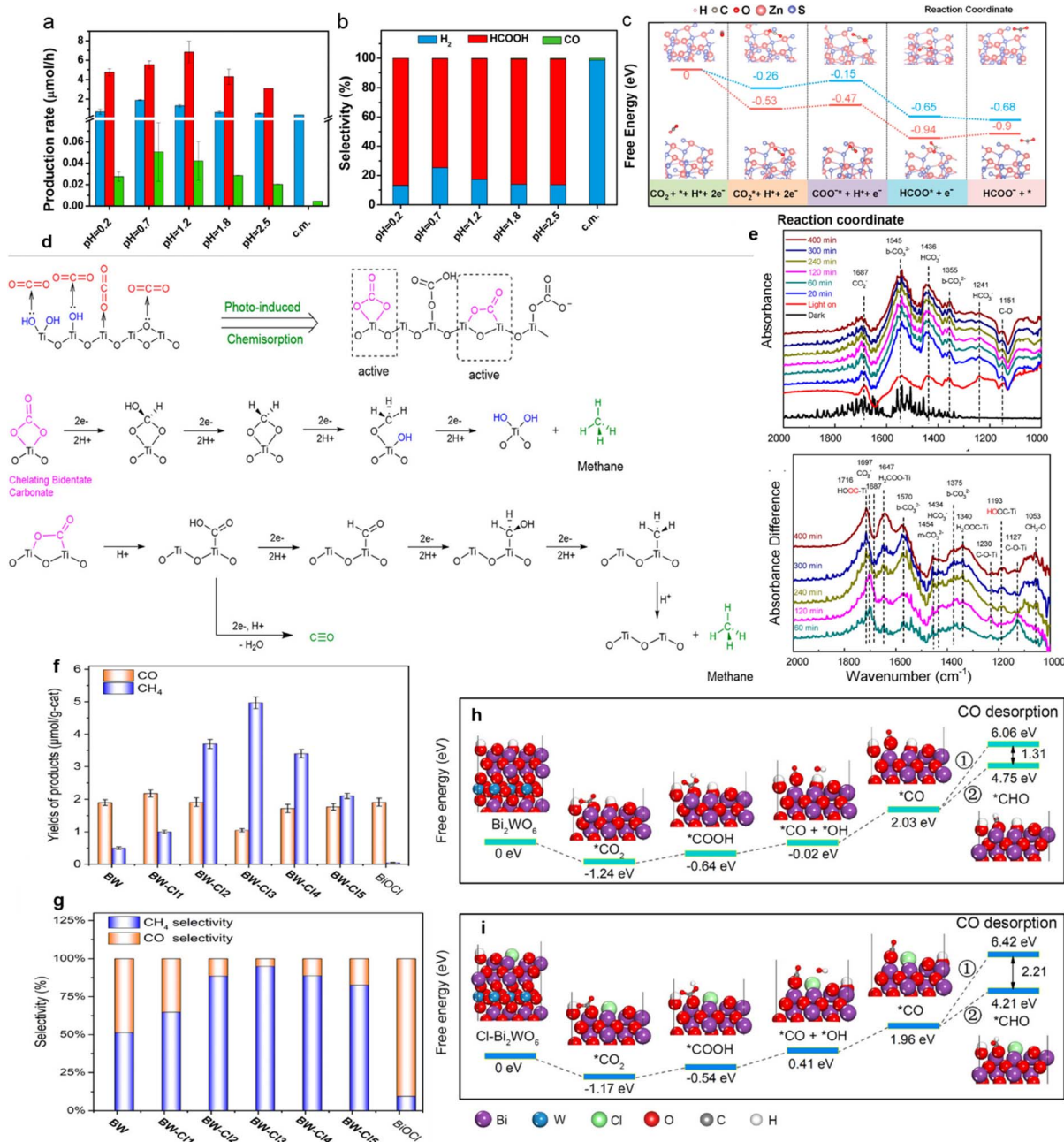


Fig. 9 (a) Yields and (b) selectivity of HCOOH, CO, H₂ over ZnS samples etched by sulfuric acid of different pH values. (c) Free energy diagram for the pathways of CO₂ conversion to formate on a perfect ZnS (blue) and V_{Zn}-ZnS (pink) surface. Reproduced with permission from ref. 134 copyright 2019 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 = 1–5) 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 CO₂ reduction over TiO₂, g-C₃N₄ and BiOBr with or without Pt loading. (b) CO-TPD of TiO₂ and Pt-TiO₂. Reproduced with permission from ref. 58 copyright 2018 Royal Society of Chemistry. (c) The evolution rates and the selectivity of CO and CH₄ over TiO₂ and various HAP/TiO₂ photocatalysts. (d) A possible pathway for the conversion of CO₂ to CH₄ over Pt/HAP/TiO₂ in the presence of H₂O. *In situ* IR spectra of (e) Pt/HAP/TiO₂ and (f) Pt/TiO₂.⁶⁸ Reproduced with permission from ref. 68 copyright 2018 Elsevier. (g) Schematic illustration of the photocatalytic CO₂ conversion to CH₄ 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 → Ti-CHO → Ti-CH₂OH → Ti-CH₃ → CH₄ to produce CH₄ (Fig. 9e).¹³⁵

Ion modification can also improve the selectivity of CO₂ reduction by adjusting the formation energy of key intermediates.¹³⁸ Li prepared Bi₂WO₆ (BW) nanosheets loaded with different amounts of Cl⁻ ions, which were marked as BW-Cl_x (x = 1–5).⁷⁰ A maximum selectivity of 94.98% for CH₄ generation was achieved on the surface of BW-Cl₃ (Fig. 9f and g).⁷⁰ In the

presence of Cl⁻ ions, the half-reaction (*i.e.*, oxygen evolution) of Bi₂WO₆ nanosheets was greatly increased.⁷⁰ Simultaneously, the produced protons facilitated the formation of CH₄.⁷⁰ Moreover, DFT calculations (Fig. 9h and i) confirmed that the presence of Cl⁻ ions on Bi₂WO₆ nanosheets was capable of lowering the energy barrier for the generation of crucial intermediate (*i.e.*, *CHO), thus enhancing CH₄ production.⁷⁰

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 CH_4 , and it should be guaranteed that not only the formation energy of *CHO is low, but also *CHO is stable enough to generate CH_4 . 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 CH_4 generation was achieved by loading 1% Pt on the TiO_2 , C_3N_4 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 CH_4 and the Pt clusters, CH_4 exhibited low adsorption energy on the Pt clusters, leading to the easy desorption of generated CH_4 from the Pt surface.⁵⁸ Thus, most CO products produced during the photocatalytic process were anchored on the catalyst surfaces, and CH_4 molecules were desorbed from the photocatalyst surface, eventually achieving enhanced selectivity of CH_4 generation.⁵⁸

Through compound modification of the catalysts, the stability of some key intermediates can also be improved. Hydroxyapatite (HAP)-decorated TiO_2 could achieve 99.1% selectivity of CH_4 generation (Fig. 10c).⁶⁸ The formation of much more stable intermediates over HAP/ TiO_2 nanorods was responsible for this selectivity enhancement.⁶⁸ A possible pathway for the conversion of CO_2 to CH_4 over Pt/HAP/ TiO_2 in the presence of H_2O is proposed in Fig. 10d.⁶⁸ Specifically, the formate-like species ($HCOO^-$) was identified as the crucial intermediate for CH_4 production.⁶⁸ Compared with that of TiO_2 , IR peaks at $3000\text{--}2800\text{ cm}^{-1}$ of Pt/HAP/ TiO_2 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 Ti_3C_2 could dramatically enhance the evolution rate of CH_4 ($16.61\ \mu\text{mol g}^{-1}\text{ h}^{-1}$),¹⁴² in which surface hydroxyls on selective CH_4 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 CO_2 , which is critical to the CO_2 activation.¹⁴¹ Moreover, the intermediates could be stabilized by forming hydrogen bonds between the

intermediates and $-OH$ groups. These effects improved the selective CH_4 generation.¹⁴¹

Although the stability of the intermediates remarkably affects the reaction path of photocatalytic CO_2 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 CO_2 reduction more comprehensive and convincing.

3.3. Desorption of products

As one critical step in the entire CO_2 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 (V_{Bi}).¹⁴⁴ Compared with $BiOBr$ nanosheets without V_{Bi} , CO could be more easily desorbed from the surface of $V_{Bi}\text{-}BiOBr$, 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 CO_2 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

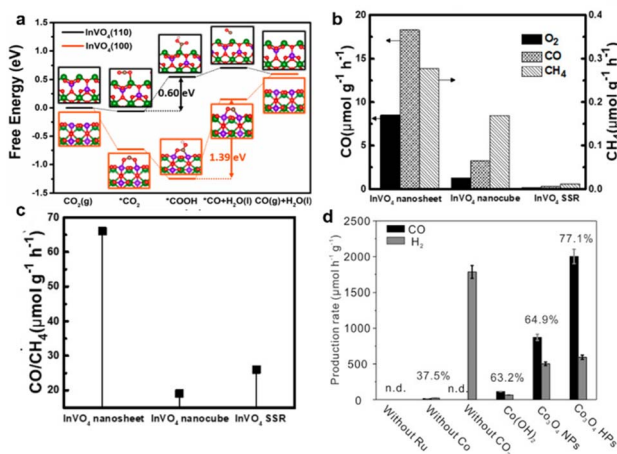


Fig. 11 (a) The photocatalytic activity and (b) the production rates of CO to CH_4 over the ultrathin $InVO_4$ nanosheets, nanocubes, and obtained by SSR. (c) Calculated Gibbs free energy profiles of photocatalytic CO_2 reduction to CO over $InVO_4$ of the (110) and (100) planes, respectively. Reproduced with permission from ref. 148 copyright 2019 American Chemical Society. (d) Photocatalytic production rate using $\beta\text{-}Co(OH)_2$, Co_3O_4 nanoparticles (Co_3O_4 NPs), or Co_3O_4 hexagonal platelets (Co_3O_4 HPs) as catalysts under visible light ($\lambda > 420\text{ nm}$) 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.¹⁴⁸ 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).¹⁴⁸ 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).¹⁴⁹

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 non-metal 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%.⁸¹ 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 CO₂.⁸¹ This synergy increased photocatalytic production selectivity.⁸¹ 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 half-reaction and the oxidation half-reaction since how photo-induced 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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