

Engineered TiO₂ Nanocatalysts for Photocatalytic Methane Conversion: Modification Strategies, Reactor Engineering, and Mechanistic Insights

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Abstract: Photocatalytic methane conversion provides a sustainable way to convert abundant methane resources into high value-added chemicals under mild conditions. Photocatalysts based on titanium dioxide (TiO₂) have attracted much attention for their high stability, low cost and suitable electronic structure. However, the inefficiency and poor product selectivity of the original TiO₂ seriously limit its practical application. This paper systematically reviews the research progress of TiO₂-based photocatalysts in methane conversion in recent years from two complementary perspectives. First of all, the five main catalyst modification strategies are discussed in detail, including crystal facet engineering, doping and defect engineering, catalyst modification, porous structure construction and heterojunction engineering, with emphasis on their roles in regulating charge separation, surface reaction pathways, and intermediate conversion. These strategies significantly improve the performance of catalysts. For example, on Pd-O_v co-modified TiO₂, the yield of C₁ oxygen-containing compounds is as high as 54,693 μmol g⁻¹ h⁻¹, and the selectivity is close to 100%. Secondly, this article focuses on the latest progress of reactor engineering and advanced in-situ characterization technology, and explains how the reaction environment, mass transfer process and mechanism analysis jointly promote the practical application of photocatalytic methane conversion. Finally, this paper discusses the challenges and future prospects of high-efficiency selective methane conversion, aiming to guide the development of the next-generation titanium dioxide-based photocatalytic system.

Keywords: photocatalysis; methane conversion; TiO₂-based photocatalyst; modification strategy; product selectivity

1. Introduction

Methane is the main component of natural gas, shale gas, coal seam gas and natural gas hydrate, and it is also the most abundant single carbon resource in nature [1–3]. In the process of global transformation to a low-carbon energy structure, its direct conversion into high-value chemicals is an important way for carbon recycling. At the same time, methane is also a powerful greenhouse gas, with a global warming potential value of about 28 times that of carbon dioxide [4,5]. Therefore, efficient methane value-added utilization technology is crucial to mitigate climate change and achieve sustainable energy supply [6–15]. Traditional methane conversion relies on high-energy-consuming thermal catalytic processes [16,17], such as steam methane reforming (SMR) or dry reforming of methane (DRM), which are usually carried out at temperatures above 700 °C. These processes not only consume



a large amount of fossil fuels, but also are accompanied by significant secondary carbon dioxide emissions. Therefore, the development of methane conversion replacement technology under mild conditions has become a very attractive green path.

Photocatalysis uses photon energy to produce high-energy carriers, which can directly participate in the electron transfer process [18–26]. This process enables the transformation subject to thermodynamic restrictions under mild conditions [27]. After light excitation, semiconductors produce oxidative holes and reducing electrons, thus promoting the generation of reactive oxygen (ROS), such as $\bullet\text{OH}$ and $\bullet\text{O}_2^-$ [28]. These active species trigger CH_4 dehydrogenation to produce $\bullet\text{CH}_3$. The subsequent reaction path changes with the reaction environment. Under anaerobic conditions, $\bullet\text{CH}_3$ undergoes a coupling reaction to achieve non-oxidation coupling (NOCM) of methane, generating C_2H_6 and H_2 [29–31]. In an oxidation atmosphere, the reaction can lead to the oxidation coupling (OCM) of methane [32–34] or the partial oxidation of methane (POM), thus producing liquid oxygenated compounds with high added value (CH_3OOH , CH_3OH , HCHO , $\text{C}_2\text{H}_5\text{OH}$, etc.) [35–37]. These diversified catalytic pathways together form a multifunctional platform that can be used to sustainably upgrade methane to high-value chemical raw materials.

Since Fujishima and Honda pioneered the photocatalytic hydrolysis reaction on TiO_2 electrodes under ultraviolet irradiation in 1972 [38], TiO_2 has become one of the most widely studied semiconductor photocatalysts and a benchmark material in the field of photocatalysis [39]. In particular, in recent years, research on TiO_2 in methane conversion has developed rapidly, which can be seen from the publication trend of annual papers in this field (Figure 1). TiO_2 has attracted attention not only for its non-toxic, low cost and excellent photocorrosion resistance, but also for its mature structure and stable crystal and electronic structure, making it an ideal platform for mechanism research and catalyst design [40,41]. In photocatalytic methane transformation, the high positive valence band of TiO_2 provides sufficient oxidation capacity to activate the inert C–H bond in methane, and its conduction band can drive oxygen activation and related reduction processes, thus producing reactive oxygen species that participate in subsequent methane conversion steps. In addition, the surface and interface properties of TiO_2 can be flexibly regulated by methods such as defect engineering, heteroatomic doping, crystal surface regulation and cocatalyst loading, which provides rich opportunities for regulating charge separation and reaction path [42,43]. However, pure TiO_2 still has some inherent limitations, including its broadband gap (3.2 eV for the sharp titanium type and 3.0 eV for the rutile type), low visible light utilization rate and fast charge carrier recombination [44,45]. In addition, the high oxidation of TiO_2 usually makes it difficult to accurately control ROS and carbon-containing intermediates (such as $\bullet\text{OCH}_3$), resulting in excessive oxidation to produce CO_2 and poor product selectivity.

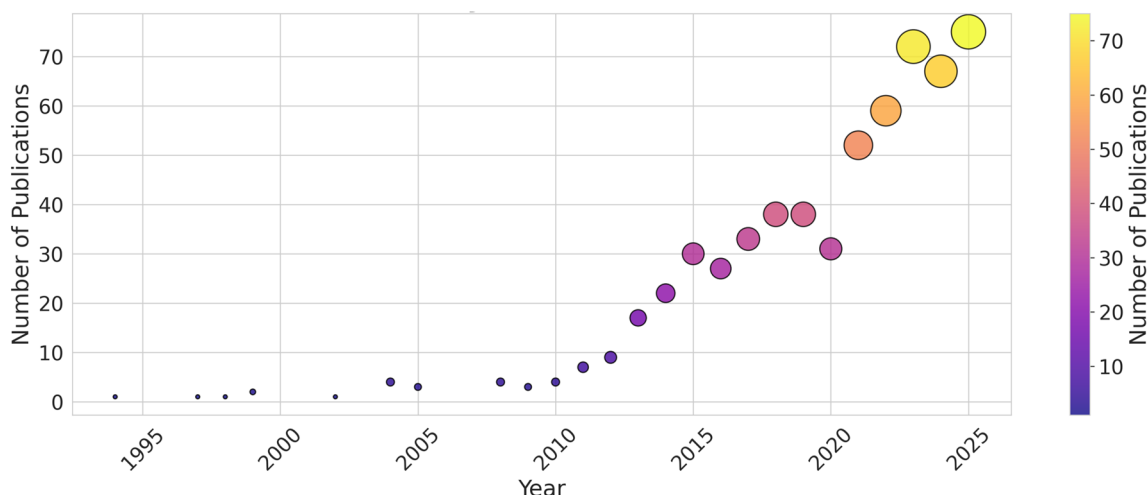


Figure 1. The trend in the number of publications in the field of TiO_2 -based photocatalytic methane conversion since 1994 (Source: Web of Science).

In view of these challenges, reasonable modification strategies have become the core research direction that gives TiO_2 high-efficiency methane conversion ability and higher product selectivity. This review systematically summarizes the research progress of modified TiO_2 -based photocatalysts in methane conversion in recent years. The article discusses in detail the five main strategies, including crystal facet engineering, doping and defect engineering, cocatalyst modification, porous structure and heterojunction construction. It focuses on how these methods regulate the electronic structure and interface environment, so as to achieve the control of charge kinetics

and intermediates. In addition, the innovation of reactor design and the progress of in-situ characterization technology are highlighted, and their key role in clarifying the reaction mechanism and promoting industrial applications is emphasized. Finally, this review looks forward to future opportunities and challenges, which provides a prospect for the sustainable development of this field.

2. Challenges in Photocatalytic Methane Conversion

Although photocatalysis technology provides a promising strategy for methane conversion at normal temperature and pressure, the field is still in the exploration stage. The inherent inertness of methane and the complexity of the interface reaction path limit the reaction process, resulting in many challenges in the clarification of the activation mechanism and the selective control of products.

Methane is the simplest hydrocarbon molecule, with a highly symmetrical tetrahedral structure, composed of sp^3 hybridized orbitals and four equivalent C–H bonds (Figure 2a) [46]. The very small electronegative difference between carbon (C, 2.55) and hydrogen (H, 2.20) leads to its extremely low polarizability ($2.84 \times 10^{-40} \text{ C}^2 \text{ m}^2 \text{ J}^{-1}$) [47,48], making it difficult to produce effective polarization under external electric field or interface interaction. Therefore, the molecule shows significant inertia in both electrophilic and nucleophilic attacks. From the perspective of molecular orbital, methane lacks both low-energy unoccupied orbitals and high-energy occupied orbitals, making electron extraction or injection energy-disadvantaged [49–51]. These electronic properties give CH_4 excellent chemical stability and also bring major challenges to the activation of C–H bonds under mild conditions. Although a variety of activation mechanisms have been proposed, including hole-induced hydrogen extraction [52–54], electron-induced C–H bond cleavage [55,56], metal–methyl interaction [57–59] and free radical-mediated activation [60,61], these mechanisms in different catalytic systems often coexist and compete with each other, which makes it complicated to determine its internal activation path.

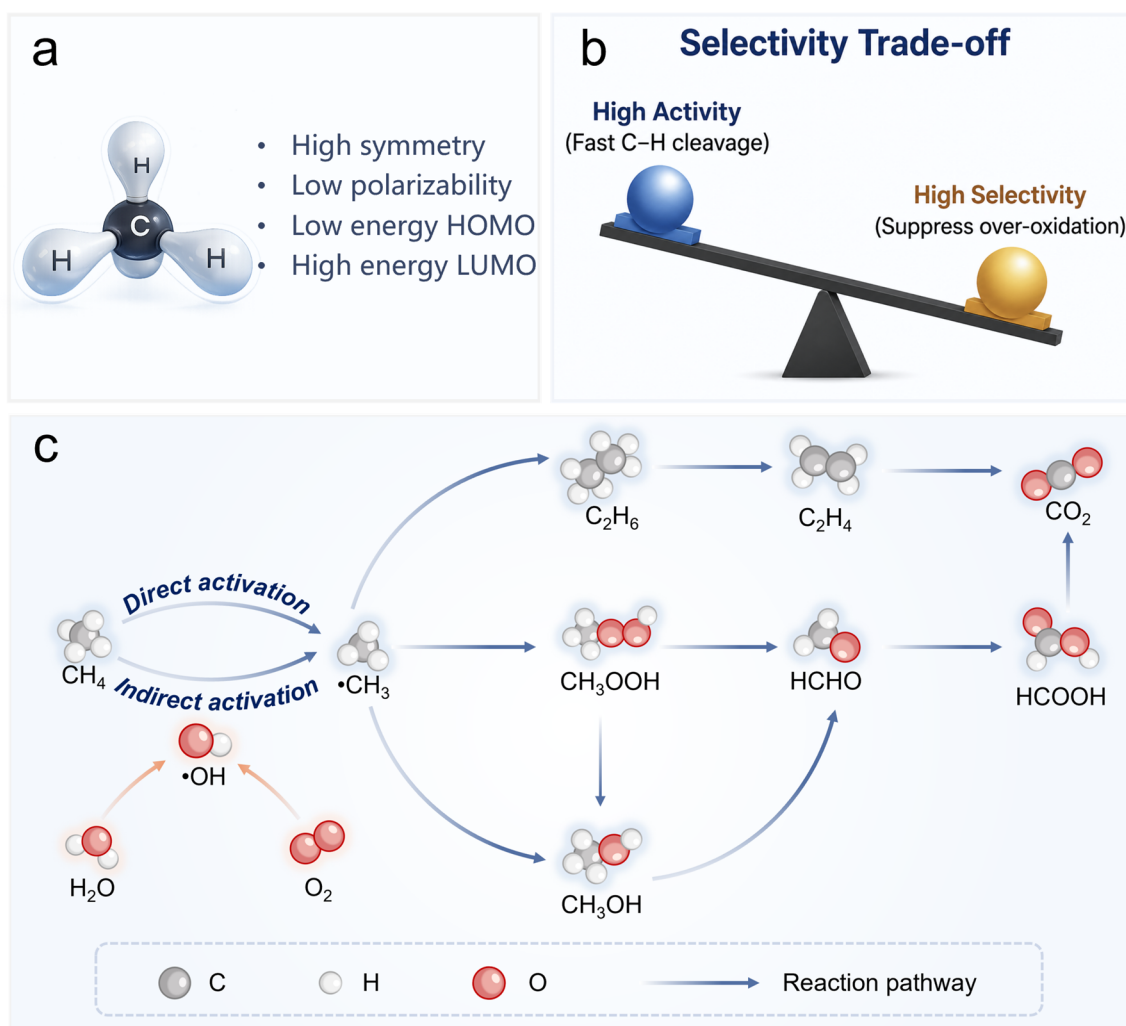


Figure 2. (a) The symmetric tetrahedral structure of methane. (b) Schematic diagram of photocatalytic methane oxidation activity-selective trade-off. (c) Schematic diagram of the general reaction path of photocatalytic CH_4 transformation.

Another important bottleneck in photocatalytic methane conversion is that primary products are usually more reactive than methane [62–64]. For example, the C–H bond dissociation energy of CH₃OH is about 0.4 eV lower than that of CH₄ [65,66], making it easier to be continuously oxidized into CO₂ under strong oxidation conditions. The priority reaction activity of this intermediate inevitably leads to a sharp decline in the selectivity of the target product (Figure 2b). In addition, there are multiple parallel or continuous reaction paths in the photocatalytic system (Figure 2c) [67], including free radical chain reaction, lattice oxygen-mediated oxidation reaction and metal site-driven coupling reaction, which makes the reaction network highly complex. Although the reaction path mediated by radicals can effectively reduce the energy barrier of C–H bond fracture and improve the overall reaction rate, its randomness and high reaction activity make it difficult to precisely control the distribution of products. This usually leads to selective trade-offs between various products (such as CH₃OOH, CH₃OH, HCOOH and HCHO). Therefore, the core challenge in this field is to maintain high catalytic activity while inhibiting excessive oxidation, stabilizing key intermediates, and guiding them to transform along the required path.

3. Modification Strategy of TiO₂

3.1. Facet Engineering

Due to its excellent stability and rich reserves, TiO₂ has attracted wide attention in the field of photocatalysis. It is worth noting that the surface-dependent catalytic performance caused by its polycrystalline structure has become the main research direction. The anatase and rutile phases expose typical low-index crystal planes, such as {001}, {101}, and {110}, each with a unique atomic arrangement, coordination environment, and electronic structure. These intrinsic differences directly lead to significant differences in methane adsorption, interface charge transfer kinetics and overall catalytic activity [42,68]. For example, the anatase {001} facet shows higher reactivity due to the abundant content of five-coordinated unsaturated Ti (Ti_{5c}) atoms [69–71], while the {101} facet is still the most thermodynamically stable and dominant crystal surface in the synthesized TiO₂ sample [72]. In the rutile structure, the {110} facet is the main exposed surface, which plays a decisive role in the charge carrier transmission and surface reaction [73].

Based on these basic understandings, facet engineering has been proven to directly regulate charge dynamics and reaction pathways. Uniform anatase nanocrystals surrounded by specific crystal faces indicate that the {001} surface can induce spontaneous bulk-surface charge separation [74], in which photogenerated holes are enriched on the surface while electrons migrate into the bulk phase. This built-in charge carrier spatial separation significantly enhances the transfer of interfacial holes to adsorbed methane, thereby endowing it with higher catalytic activity than nanocrystals that primarily expose {100} or {101} crystal facets. Although this study mainly reports that CH₄ is completely oxidized to CO₂ rather than the generation of selective oxygenated compounds, it remains a valuable example of how the exposed TiO₂ crystal surface regulates charge separation and methane activation behavior.

In addition to these inherent characteristics, selectively loading cocatalysts or building crystal facet junctions provide a more advanced method to regulate the reaction pathways. Cocatalysts are usually deposited to a specific facet by photodeposition, which uses the internal electric field of the semiconductor to guide the carrier to a specific surface. For example, Chang et al. synthesized Au/TiO₂ catalysts by chemical reduction and photodeposition [75], achieving non-selective and facet-selective Au deposition, respectively. Mechanistic studies show that Au deposited on the {001} facet promotes the activation of •O₂[−] to •OH (Figure 3a), which is conducive to the generation of CH₃OH. On the contrary, Au anchored on the {101} facet promotes •O₂[−] protonation to •OOH, guiding the reaction to produce CH₃OOH. In addition, Hu et al. synthesized anatase TiO₂ with an adjustable {001}/{101} facet ratio via by HF-regulated hydrothermal method [76]. The junction of 62% {001} facet and 38% {101} facet maximizes the driving force of spatial charge separation, while achieving the optimal *OCH₃/•OH ratio. This synergy effect inhibits the excessive oxidation to CO₂ induced by •OH, ultimately achieving the highest yield and selectivity of HCHO.

The more fundamental dimension of facet engineering lies in the intrinsic structural characteristics of different crystal surfaces, which determine the thermodynamics of defect formation, thus regulating the catalytic pathways and product distribution. Specifically, compared with the thermodynamically stable {101} facet, the high surface energy and distorted lattice of the anatase {001} facet significantly reduce the formation energy of photogenerated oxygen vacancy. The research of Ye et al. shows that selectively loading Ag onto the TiO₂{101} facet can promote the enrichment of holes on the {001} facet, thus inducing the formation of oxygen vacancies [77]. These vacancies can stabilize the superoxide radicals into surface peroxides (Figure 3b), while avoiding the generation of free •CH₃ and •OH, which are the main driving factors for over-oxidation on the {101} facet.

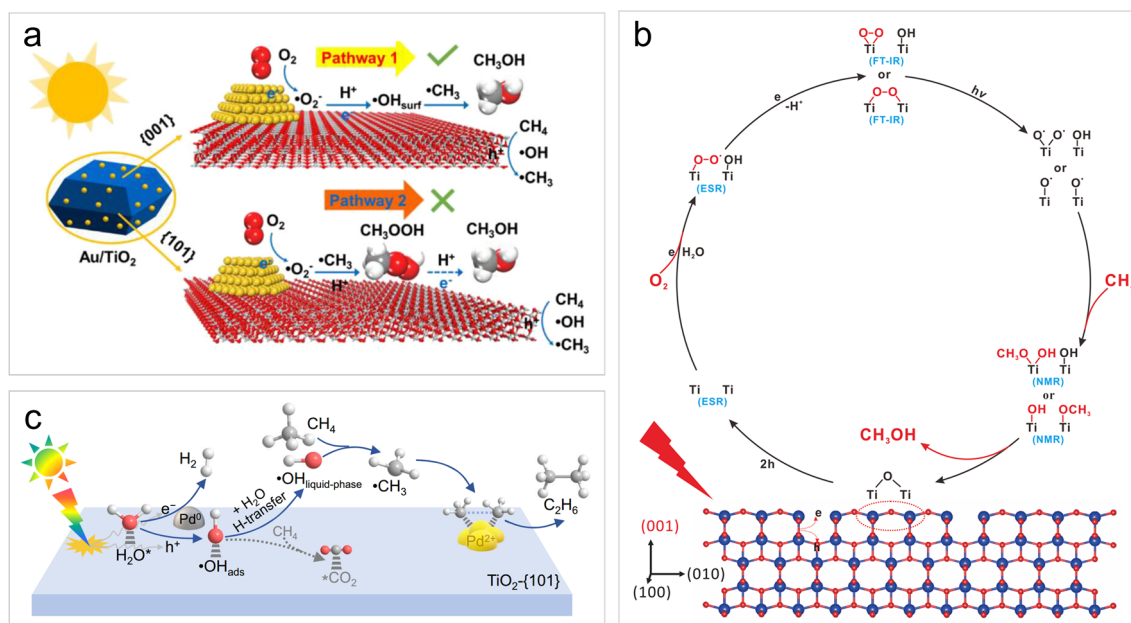


Figure 3. (a) Proposed catalytic mechanism for the oxidation of methane over Au/TiO₂ [75] Copyright 2024, American Chemical Society. (b) Proposed photocatalytic mechanism for CH₄ oxidation by O₂ on the {001} facets of TiO₂ [77] Copyright 2021, Springer Nature. (c) Mechanism for photocatalytic NOCM with H₂O on Pd/TiO₂-{101} [78] Copyright 2024, Springer Nature.

Although the high-energy {001} facet is usually considered to be more reactive, Wang et al. found that the thermodynamically stable {101} facet of anatase TiO₂ exhibit superior activity and C₂ selectivity in the aqueous non-oxidative coupling of methane (NOCM) [78]. This anomalous facet effect stems from the mechanism by which the {101} facets promote the release of •OH into the liquid phase through hydrogen transfer (Figure 3c), thus effectively activating CH₄ into •CH₃. In contrast, the high-energy {001} facet undergo over-oxidation due to the strong adsorption of •OH, resulting in deep oxidation to produce CO₂. In summary, these studies emphasize that facet engineering not only controls charge separation and defect thermodynamics, but also determines abnormal reaction activity phenomena. These findings highlight the need to re-evaluate the traditional assumption about the inherent advantages of high-energy facets. Ultimately, these facet-dependent strategies become powerful tools for designing selective photocatalysts for methane conversion. Table 1 summarizes the representative research of facet-engineered TiO₂ photocatalyst for methane conversion.

Table 1. Comparative summary of TiO₂-based facet engineering in photocatalytic methane conversion.

Catalyst	Reactants	Light source	Products	Ref.
Anatase TiO ₂ {001}	Gas phase flow-bed, 0.15 atm CH ₄ , 0.05 atm O ₂	70 W LED, 365 nm	CO ₂ (CH ₄ combustion, 17.6 mmol g ⁻¹ h ⁻¹)	[74]
Au/TiO ₂ {001}/{101}	Liquid phase, 2.0 MPa CH ₄ , 0.04–0.8 MPa O ₂	300 W Xe lamp, 350–780 nm	CH ₃ OH ({001}), CH ₃ OOH ({101}), HCHO, CO ₂	[75]
Bare anatase TiO ₂ {001}/{101} junction	Liquid phase, 21 bar CH ₄ , 1 bar O ₂	365 nm LED or 300 W Xe lamp	HCHO (280 mmol g ⁻¹ h ⁻¹ L ⁻¹ , 100% selectivity)	[76]
Ag/TiO ₂ {001}/{101}	Liquid phase, 2.0 MPa CH ₄ , 0.1 MPa O ₂	300 W Xe lamp, 450 mW cm ⁻²	CH ₃ OH (4.8 mmol g ⁻¹ h ⁻¹ , ~80% selectivity)	[77]
Pd/TiO ₂ {101}	Liquid phase NOCM, CH ₄ , H ₂ O, ambient pressure	300 W Xe lamp, 320–780 nm	C ₂ H ₆ (262 μmol g ⁻¹ h ⁻¹), C ₂ H ₄ , H ₂ , minor CO ₂ (81% C ₂ selectivity)	[78]

Note: cross-comparisons between entries should be made with caution given the disparate reaction conditions.

3.2. Doping and Defect Engineering

Doping and defect engineering is the basic strategy to regulate the natural behaviour of TiO₂ [79–83]. The electronic band structure of TiO₂ may be accurately controlled by substitutional or interstitial doping with heteroatoms in the lattice [84,85]. As an illustration, non-metallic dopants like C, N and S tend to introduce the

band gap intermediate state near the valence band edge (O 2p) to narrow the band gap and extended the region of light absorption to visible light [41]. On the other hand, metal doping can enhance the conductivity and regulate the redox potential, which helps in facilitating the migration and separation of photocarriers.

Early studies have been mostly aimed at single element doping to maximize the optical behavior and charge separation. As regards non-metallic modification, Jiang et al. prepared N-doped anatase/rutile hybrid crystal TiO₂ by one-step air calcination of TiN [86]. Nitrogen doping can decrease the band gap and improve the light capture ability. Simultaneously, the cooperation with interface phase promotes the adsorption of H₂O and controlled generation of •OH, which facilitates the selective oxidation of CH₄ into HCHO. Regarding metal modification, W-doped TiO₂ photocatalyst prepared by hydrothermal method achieves highly selective methane oxidation [87]. Besides narrowing the band gap, W doping also induced an upward shift of the band structure, so that the valence band is lower than the oxidation potential of H₂O/•OH. This electronic regulation effectively inhibits excessive •OH generation and reduces the selectivity of CO_x from 21.2% to 0.6%.

In order to further optimize the local electronic environment, researchers have developed co-doping strategies to take advantage of the complementary properties of various heteroatoms. One interesting case is the synthesis of ultra-thin TiO₂ nanosheets co-doped with Cu and Si by solvothermal method [88]. In the dual-doped system, the introduction of Si enhances structural stability and balances lattice distortion, whereas the Cu species serves as the redox activity center (Cu²⁺/Cu⁺) to promote the formation of O_v and Ti³⁺ species. This synergistic effect of dual doping reduces the energy barrier of CH₄ adsorption and C–H bond activation.

Surface defect engineering provides an alternative approach to construct coordinatively unsaturated sites to activate reactants. Luo et al. (Figure 4a) constructed an O_v-rich disordered layer on the TiO₂ surface by heat treatment in an H₂ reduction atmosphere [89]. The investigation showed that the optimized 1.37 nm defect layer can maximize the spatial separation of charge carriers. Meanwhile, the surface O_v may also serve as the active center of O₂ and CH₄ activation, achieving a HCHO yield of 3.16 mmol g⁻¹ h⁻¹ and a selectivity of 81.2%. Moreover, O_v can also combine with metal nanoparticles to achieve a synergistic effect. In Pd–O_v co-modified TiO₂ [90], Pd nanoparticles play the role of hole acceptors whereas O_v acts as electron traps (Figure 4b), effectively inhibiting charge recombination and enhancing the activation of O₂ and CH₄. This mechanism makes the yield of C₁ oxygenates extremely high, reaching 54,693 μmol g⁻¹ h⁻¹ with nearly 100% selectivity under mild conditions. The latest research progress highlights the combination of doping and defect engineering through innovative processes. Zhang et al. combined N₂ plasma pretreatment with photoinduced defect engineering (Figure 4c) to introduce interstitial N and controllable O_v into TiO₂ [91]. Plasma pretreatment effectively reduces the generation energy of O_v. Nitrogen doping expands the response range of visible light, while O_v accelerates charge separation and enhances the activation of O₂/CH₄ (Figure 4d). Compared with the original TiO₂, this dual defect strategy increases the methane conversion rate by 44 times, proving the powerful ability to combine heteroatomic doping with precise defect control.

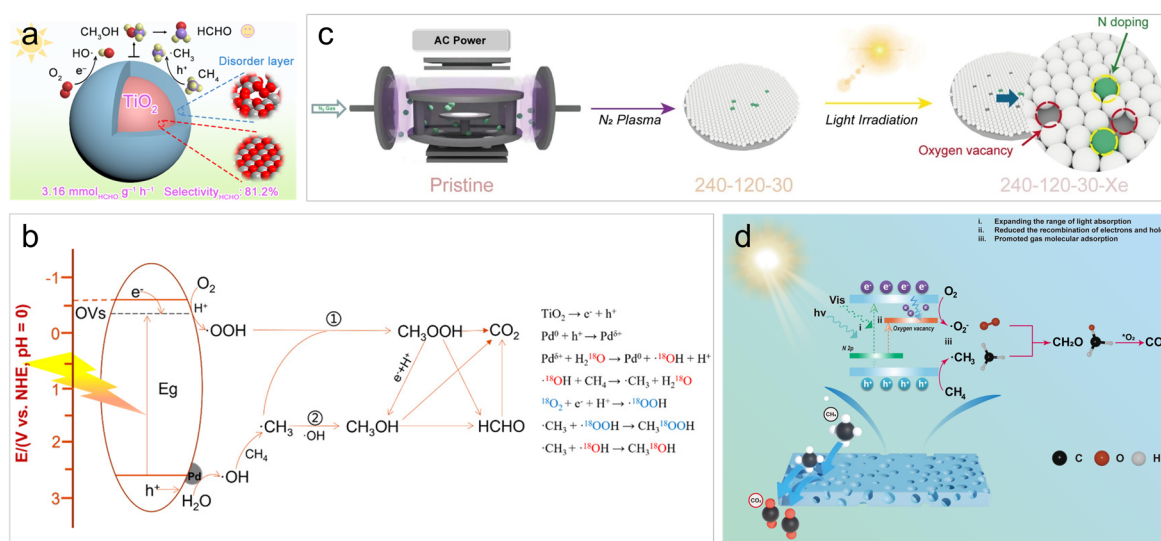


Figure 4. (a) Schematic diagram of the reaction mechanism of aerobic photocatalytic conversion of CH₄ to HCHO [89] Copyright 2022, American Chemical Society. (b) Reaction mechanism of photocatalytic transformation of CH₄ on Pd_{0.5}-def-TiO₂ [90] Copyright 2022, Wiley-VCH. (c) Schematic diagram of the synthesis process of N-TiO_{2-x} [91] Copyright 2024, Elsevier. (d) Photocatalytic mechanism for the oxidation of CH₄ over dual-defect TiO₂ with O₂ [91] Copyright 2024, Elsevier.

By combining heteroatomic doping with precise defect control, researchers have made significant improvements in light absorption, charge separation and methane activation, thus achieving higher activity and selectivity under mild conditions. Future research should give priority to the design of controllable and reversible defect doping structures, and combine advanced in situ characterization technology to track the dynamic evolution of active sites and reactive species at the atomic scale. These efforts are crucial to the design of efficient and stable methane conversion photocatalysts. Table 2 lists the typical catalytic properties of doping and defective engineering TiO₂ photocatalysts.

Table 2. Comparative summary of TiO₂-based doping and defect engineering in photocatalytic methane conversion.

Catalyst	Reactants	Light Source	Products	Ref.
N-doped anatase/rutile TiO ₂	Liquid phase, 1.9 MPa CH ₄ , 0.1 MPa O ₂	365 nm LED, 100 mW cm ⁻²	HCHO (23.5 mmol g ⁻¹ h ⁻¹ , 90% selectivity)	[86]
W-doped TiO ₂ (5.3% W)	Liquid phase, 2.0 MPa CH ₄ , 0.2 MPa O ₂	300 W Xe lamp, 350–760 nm	C ₁ oxygenates (12.2 mmol g ⁻¹ , 99.4% selectivity)	[87]
Cu and Si co-doped TiO ₂ nanosheets	CH ₄ saturated H ₂ O (ambient pressure)	300 W Xe lamp	C ₂ H ₆ (33.8 μmol g ⁻¹ h ⁻¹ , 88.4% selectivity)	[88]
Surface O _v -rich TiO ₂	Liquid phase, 1.9 MPa CH ₄ , 0.1 MPa O ₂	300 W Xe lamp	HCHO (3.16 mmol g ⁻¹ h ⁻¹ , 81.2% selectivity)	[89]
Pd and O _v co-modified TiO ₂	Liquid phase, 2.0 MPa CH ₄ , 0.1 MPa O ₂	365 nm LED, 100 mW cm ⁻²	C ₁ oxygenates (54 693 μmol g ⁻¹ h ⁻¹ , ~100% selectivity)	[90]
N-doped TiO _{2-x}	CH ₄ (ppm level), O ₂ (trace)	300 W Xe lamp, simulated sunlight	CO ₂ (4.84 μmol h ⁻¹)	[91]

Note: cross-comparisons between entries should be made with caution given the disparate reaction conditions.

3.3. Cocatalyst Modification

Despite the excellent stability of TiO₂, its performance is still limited by low charge separation efficiency and high C–H bond activation energy barrier. The introduction of cocatalysts can not only build Schottky barriers or heterojunctions at the interface, thus providing a directional charge migration channel and prolonging the carrier life [92–94], but also as a specific active site [95–98]. By regulating the adsorption energy and reaction path of key intermediates, cocatalysts can effectively lower the activation energy barrier and inhibit excessive oxidation. Therefore, the introduction of cocatalysts has become a key strategy to achieve high-efficiency methane conversion and regulate the distribution of products.

In photocatalytic systems, noble metal cocatalysts are generally considered to be electron-rich sites [99]. This is due to the difference in the Fermi energy level between the metal and the semiconductor, which drives photogenerated electrons to migrate and gather on the metal surface, thus effectively inhibiting charge recombination. For example, Lang et al. reported that Au/TiO₂ shows excellent performance in NOCM reaction in continuous flow reactors [100]. The superior performance of the system comes from the rapid transfer of photoelectrons from TiO₂ to Au nanoparticles. This efficient charge separation provides abundant active electrons for subsequent reactions. Although precious metals are usually used as electron traps, recent studies have shown that this traditional understanding can be overturned by regulating the metal-support interaction. Li et al. used rapid sputtering to deposit Au nanoparticles with an average particle size of 5.3 nm on the TiO₂ membrane [101]. Transient absorption spectroscopy (TAS) and in-situ XPS analysis show that these sputtered Au nanoparticles act as efficient hole receptors, which prolong the life of photoelectrons on the surface of TiO₂ by 66 times (Figure 5a). At the same time, the holes accumulated on the Au nanoparticles effectively drive the adsorption of CH₄, the activation of C–H bonds and the subsequent C–C coupling reaction.

With the deepening of the understanding of active sites, the structure of the cocatalyst has developed from traditional nanoparticles to atomically dispersed single-atom and sub-nanoclusters to achieve more precise interface regulation. Sun et al. anchored Pd single atoms (SAs) onto TiO₂ with a gradient distribution of Ti³⁺ defects [102]. These Pd SAs act not only as efficient electron acceptors to facilitate O₂ activation but also synergize with the internal electric field of the support to drive the hole to migrate from the bulk to the surface (Figure 5b), which significantly improves the yield of C₁ oxygenates. In addition, Wu et al. reported a strategy using sub-nanometer MoO_x clusters anchored on TiO₂ [103]. The study shows that these MoO_x clusters build unique surface Mo–O–O peroxide active sites, which is different from the traditional free radical-mediated pathway. This mechanism effectively inhibits the generation of highly oxidizing •OH and O₂^{•-} and the excessive oxidation of

subsequent products. These studies together show that atomic-level precise control of the size and configuration environment of the co-catalyst can fundamentally change the reaction pathways.

In the design of cocatalysts, the cost-effective transition metal has a unique electronic structure, so that it can show Fenton-like catalytic activity [104–106], providing a promising alternative to precious metals. Systematic research on TiO₂ systems loaded with various metals shows that Ni/TiO₂ is an excellent catalyst that can be used to produce CH₃OH with high selectivity (Figure 5c) [107]. The Ni site at the interface acts as a specific reaction center to promote the dissociation of H₂O₂ and the controlled generation of •OH through the Fenton-like mechanism (Figure 5d). This special reaction pathway balances the oxidation intensity of the surface radicals, thus preventing excessive oxidation. In order to further improve the performance, Zhao's group confined Ni nanoparticles to O_v-rich TiO₂ nanofibers [108]. The synergistic synergy of Ni(II) species and O_v significantly accelerate the catalytic dissociation of H₂O₂, thus greatly enhancing the activation of C–H bonds. Ni(II) species synergize with surface O_v to significantly accelerate the catalytic dissociation of H₂O₂, substantially boosting C–H bond activation. Leveraging this pathway, the catalyst achieved a remarkable oxygenate yield of 2.865 mol g_{Ni}^{−1} h^{−1}, with a selectivity of more than 99%.

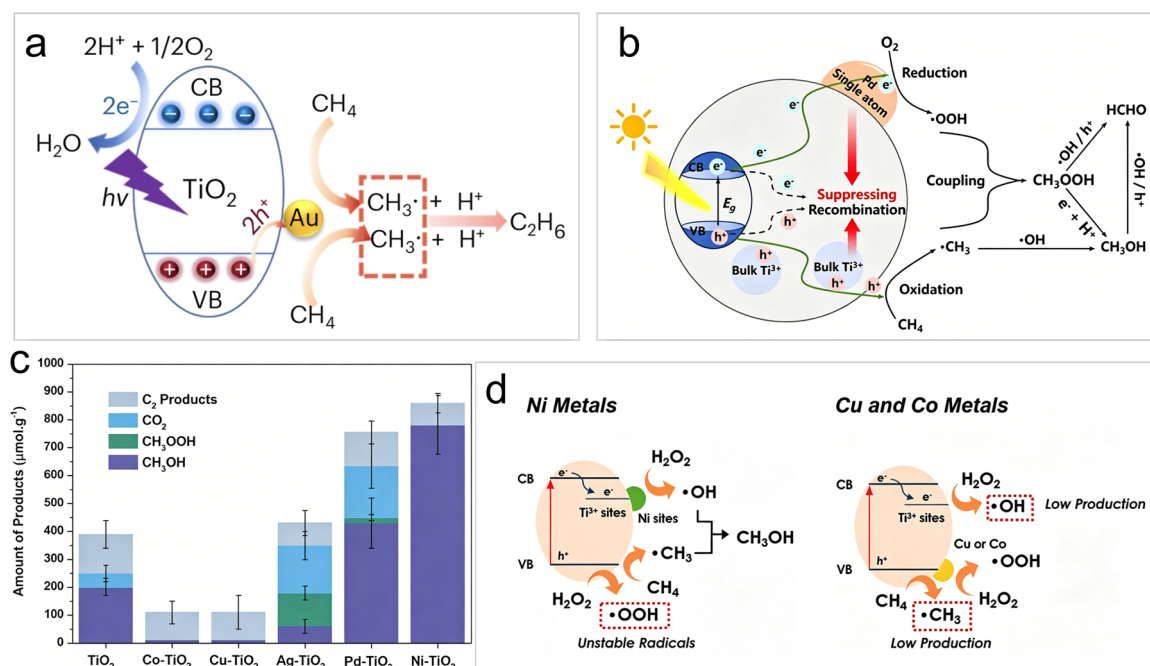


Figure 5. (a) Photocatalytic OCM process proposed on Au_{60s}/TiO₂ (after 60 s sputtering) [101] Copyright 2023, Springer Nature. (b) Schematic diagram of reaction mechanism on Pd_{0.05}/TiO₂-800 [102] Copyright 2025, Wiley-VCH. (c) Product distribution of a series of metal-modified TiO₂ samples [107] Copyright 2024, American Chemical Society. (d) Schematic representation of mechanisms for photocatalytic CH₄ oxidation. [107] Copyright 2024, American Chemical Society.

In addition to the regulation of charge carriers, cocatalysts also play a decisive role in guiding the C–C coupling pathway by stabilizing key intermediates. Specifically, the origin of C₂ selectivity has been determined to be the strong d-σ orbital hybridization between Au and •CH₃ [109]. This interaction reduces the metal–C–H bond angle, thus minimizing steric hindrance and significantly lowering the C–C coupling barrier. Based on these insights, Wu et al. further proved that •CH₃ intermediates can migrate from the support to the Au quantum dot [110], where their stabilization effectively inhibits overoxidation and promotes the generation of C₂H₆. Overall, the engineering design of cocatalysts is crucial to overcome the inherent limitations of TiO₂. Future progress will depend on atomic-level precise interface design and the development of earth-abundant transition metals to achieve sustainable and selective methane conversion. Table 3 summarizes the representative cocatalyst modified TiO₂ system for photocatalytic methane conversion.

Table 3. Comparative summary of TiO₂-based cocatalyst modification in photocatalytic methane conversion.

Catalyst	Reactants	Light source	Products	Ref.
Au-sputtered TiO ₂	CH ₄ + air, Continuous flow	365 nm LED, 100 W	1.1 mmol h ⁻¹ (CH ₄ conversion rate) 90% C ₂ selectivity	[101]
Pd SAs/TiO ₂ -800	Batch reactor, 2.0 MPa CH ₄ , 0.1 MPa O ₂	300 W Xe lamp	C ₁ oxygenates (8.14 mmol g ⁻¹ h ⁻¹ , 91.3% selectivity)	[102]
MoO _x /TiO ₂	Liquid phase, 2.0 MPa CH ₄ , 0.1 MPa O ₂	300 W Xe lamp	C ₁ oxygenates (3.8 mmol g ⁻¹ , 2 h, ~100% selectivity)	[103]
Ni-TiO ₂	CH ₄ + H ₂ O ₂ , 1 bar	UV lamps (6 × 15 W, 254 nm)	CH ₃ OH 1600 μmol g ⁻¹	[107]
Ni/TiO ₂ Nanofibers	3 MPa CH ₄ + H ₂ O ₂ , 1 bar	300W Xe lamp	C ₁ oxygenates (2.865 mol g _{Ni} ⁻¹ h ⁻¹ , 99% selectivity)	[108]
Au/TiO ₂ -O _v	CH ₄ + CO ₂ (1:1, Flow reactor)	300 W Xe lamp	C ₂ H ₆ 2.60 mmol g ⁻¹ h ⁻¹	[110]

Note: cross-comparisons between entries should be made with caution given the disparate reaction conditions.

3.4. Porous TiO₂ Architectures

At present, research in this field is still mainly focused on commercial TiO₂ nanoparticles as the main catalytic support [111,112]. However, these bulk-like materials often usually have the problem of limited active surface area and slow mass transfer, which limits the overall reaction efficiency and selectivity. In order to overcome these bottlenecks, a porous TiO₂ network has been developed to provide an expansive interfacial platform, maximize the exposure of active sites and promote the adsorption of CH₄ molecules [113–115]. In addition, these unique structures can significantly improve the light capture efficiency through multiple scattering effects and potential slow light effects in the porous framework [116–118]. By precisely tailoring the pore geometry structure, these structures can create a special microenvironment to regulate the residence time of the reaction intermediate, which effectively prevent excessive oxidation and guide the reaction to the generation of high value-added chemicals.

Using metal organic framework (MOF) to construct TiO₂ matrix structure has become an effective strategy because it can achieve highly active site dispersion and adjustable electronic state [119]. For example, MOF-derived TiO₂ can provide an ideal platform for building an interfacial dual active center, thus promoting the activation of CH₄ and O₂ [120]. Based on the versatility of MOF-derived templates, Zhang et al. designed a hollow porous Pd/H-TiO₂ nanocage for the selective oxidation of methane to methanol (Figure 6a,b) [121]. Under the same conditions, this hollow catalyst shows a CH₃OH production rate of 4.5 mmol g⁻¹ h⁻¹ with 70% selectivity, and its performance is 3.75 times that of the Pd loaded on the commercial solid TiO₂. This excellent efficiency is mainly due to its hollow structure: the thin porous shell shortens the charge migration path, thus reducing the carriers recombination; while the internal cavity enhances light capture through multiple scattering. In addition, the interconnected pore structure is conducive to the rapid diffusion of CH₃OH and effectively inhibits its excessive oxidation to CO₂.

In addition to the MOF template strategy, other advanced preparation methods have been developed to construct a special TiO₂ structure for methane conversion. For example, a mesoporous brookite TiO₂ nanorods with a uniform pore diameter (about 30 nm) was synthesized by using SiO₂ sphere as a sacrificial template [122]. This open porous structure promotes the tandem reaction pathway (CH₄ → CH₃OOH → CH₃OH), in which the CH₃OOH intermediate is efficiently reduced to CH₃OH at the Pt site, achieving a CH₃OH productivity of 883 μmol g⁻¹ h⁻¹ with 100% selectivity. In addition, an innovative hydro-crystallization constrained morphology engineering method has also been developed to prepare the hollow cubic TiO₂ structure [123]. The process involves the in-situ crystallization and subsequent thermal decomposition of NH₄Cl in sol-gel particles, thus inducing its structure to transform into a cubic geometry and produce a hollowing effect (Figure 6c,d). The obtained CuO@hcTiO₂ catalyst has a thin shell layer of 49 nm and an internal porosity of up to 91%, with a specific surface area of 408 m² g⁻¹. This structure significantly enhances light scattering and provides highly accessible active sites, enabling the non-oxidative coupling of CH₄ to C₂H₄ with an outstanding selectivity of 97.7%.

Advanced porous structures also play a decisive role in regulating the catalytic microenvironments and guiding the reaction pathway toward higher hydrocarbons. A representative study shows that embedding Au nanoparticles in a highly porous, MOF-derived TiO₂ matrix can create a special nanopore-confined microenvironment [124]. Interconnected nanopores restrict the outflow of locally generated C₂ species (Figure 6e), thereby increasing their surface coverage and residence time near the active site. When combined with in-situ vapor activation, steam activation will produce tensile strain on Au nanoparticles. The domain-limiting effect successfully stabilizes the key ethane intermediate, effectively shifting selectivity from C₂H₆ to C₃H₈. This strategy achieves a productivity

of 1.4 mmol h^{-1} with 91.3% selectivity, and an impressive apparent quantum efficiency of 39.7%. It is worth noting that the design of the next-generation porous catalyst must address the key challenge of overoxidation, because the increased residence time required for C–C coupling will also increase the risk of deep oxidation to CO_2 . Table 4 summarizes the photocatalytic properties of porous TiO_2 -based catalysts reported in recent studies.

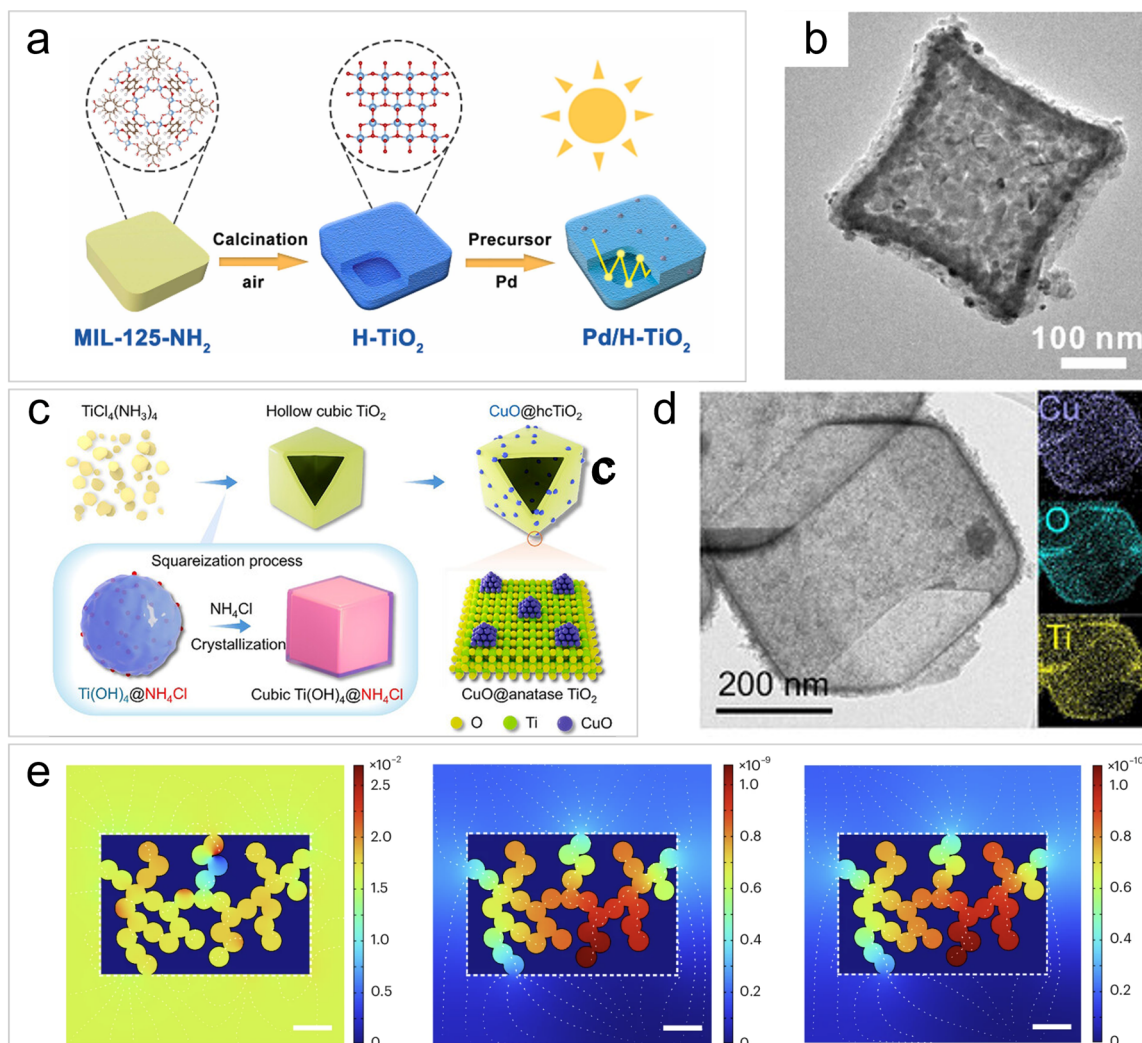


Figure 6. (a) Synthesis diagram of Pd/H-TiO₂ with porous nanocage structure [121] Copyright 2023, Elsevier. (b) Low-magnification TEM image of individual Pd/H-TiO₂ nanocage [121] Copyright 2023, Elsevier. (c) CuO@hcTiO₂ particle preparation process diagram [123] Copyright 2026, Wiley-VCH. (d) TEM image of CuO@hcTiO₂ particles [123] Copyright 2026, Wiley-VCH. (e) Computed concentrations (colour scale, in millimoles per cubic metre) and flux distributions (arrows) on the nanopore confinement structure (From left to right are CH₄, C₂H₆, and C₃H₈, respectively.) [124] Copyright 2025, Springer Nature.

Table 4. Comparison of photocatalytic methane conversion performance over different porous TiO₂ architectures.

Catalyst	Reactants	Light source	Products	Ref.
Pd/H-TiO ₂ hollow porous nanocages	CH ₄ , O ₂ , H ₂ O (3.0 MPa)	300 W Xe lamp	CH ₃ OH 4.5 mmol g ⁻¹ h ⁻¹ , 70% selectivity	[121]
Pt/brookite TiO ₂ (mesoporous)	CH ₄ + H ₂ O ₂ , 1 bar	300 W Xe lamp	CH ₃ OH 883 μmol g ⁻¹ h ⁻¹ , 100% selectivity	[122]
Hollow cubic CuO@hcTiO ₂	CH ₄ (0.4 MPa, non-oxidative)	300 W Xe lamp	C ₂ H ₄ 3937.2 μmol g _{CuO} ⁻¹ h ⁻¹ , 97.7% selectivity	[123]
Au-embedded porous TiO ₂	CH ₄ + O ₂ + H ₂ O (steam), flow reactor	Simulated sunlight	C ₃ H ₈ 1.4 mmol h ⁻¹ , 91.3% selectivity	[124]

Note: cross-comparisons between entries should be made with caution given the disparate reaction conditions.

3.5. Heterojunction Construction

Heterojunction engineering has become a key strategy to overcome the intrinsic limitations of single-component TiO_2 photocatalysts. By coupling TiO_2 with complementary semiconductors or functional materials, the matched band structures generate a built-in electric field, therefore driving the spatial separation of photoelectrons and holes [125–127]. This separation not only prolongs the carrier lifetime, but also can accurately control the redox potential of the active site. In photocatalytic methane conversion, the construction of various heterogeneous structures can finely regulate the dynamics of ROS, promoting the selective conversion into the required high value-added chemicals.

To address the challenge of excessive oxidation caused by the extremely high oxidation potential of TiO_2 valence band holes, building heterostructures with complementary components has been proven to be an effective strategy. A common method is to couple TiO_2 with metal oxides or halides with higher valence bands, guiding the photogenerated holes to migrate to a position with a lower oxidation potential. For example, modifying TiO_2 with CoO_x nanoclusters can effectively lead the hole away from the surface of TiO_2 [128]. Since the valence band of CoO_x (~2.4 V relative to NHE) is more negative than the potential required for H_2O oxidation to $\bullet\text{OH}$ (2.8 V relative to NHE), the formation of these non-selective ROS is inhibited (Figure 7a). This dual-cocatalyst system optimized with Au nanoparticles achieves up to 95% selectivity by preventing primary oxygenates (CH_3OOH and CH_3OH) from being deeply oxidized into CO_2 .

Similar regulation mechanisms have also been applied to the flow reactor system to further improve product control. Incorporating CuO_x clusters or AgBr onto TiO_2 creates heterojunctions, in which the lower oxidation potential of secondary components can protect C_2 intermediates from excessive dehydrogenation. In the bimetallic $\text{Pt-CuO}_x/\text{TiO}_2$ system [129], Pt acts as an electron trap, while CuO_x regulates the hole-driven oxidation, achieving the first success of continuous photocatalytic oxidative coupling of methane to C_2 hydrocarbons with 60% selectivity. In addition, the use of $\text{Ag-AgBr}/\text{TiO}_2$ ternary catalyst in a pressurized flow reactor significantly enhances mass transfer [130]. Using the mild oxidation environment of AgBr , this catalyst achieves a C_2H_6 yield of $35.4 \mu\text{mol h}^{-1}$ and a C_{2+} selectivity of 79%. These studies together show that the precise regulation of the interface redox potential by constructing heterojunctions is the key to achieving high selectivity of photocatalytic methane conversion.

Constructing a multi-component heterostructure can effectively regulate the redox environment, and another advanced method is phase junction engineering [131–133], which utilizes the interface between different crystal types of TiO_2 to improve charge separation. Since TiO_2 in different crystal phases has different Fermi levels and band positions, the built-in electric field generated at the phase interface is conducive to the spatial separation of charge carriers while maintaining high chemical stability. For example, Jiang et al. optimized the structure of commercial anatase TiO_2 through a simple annealing process [134], constructing a biphasic catalyst with an interface concentration of 90% anatase and 10% rutile (Figure 7b). This specific phase junction significantly enhances charge separation and extends carrier lifetimes to more than 350 ps. Mechanistic studies shows that photogenerated holes migrate to the surface of rutile to form active lattice oxygen species ($\text{O}^\bullet$), lowering the C–H bond activation barrier and promoting stable intermediate transformation. Similarly, compared with pure $\text{TiO}_2(\text{B})$, the construction of anatase/ $\text{TiO}_2(\text{B})$ homojunction nanosheets can create a milder oxidation environment [135]. With Au nanoparticles as cocatalysts to capture $\bullet\text{CH}_3$, the system has achieved a stable C_2H_6 yield of $170 \mu\text{mol g}^{-1} \text{h}^{-1}$ in the flow reactor.

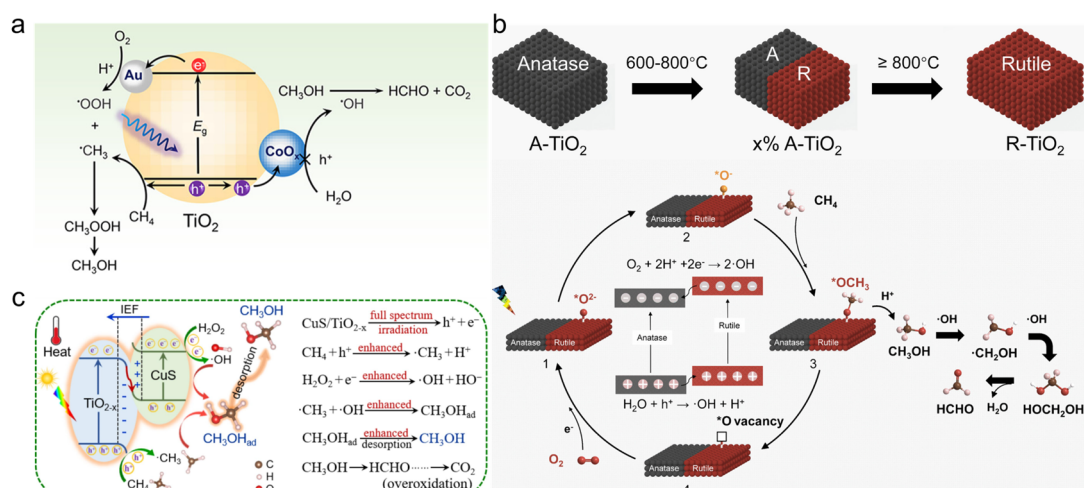


Figure 7. (a) Reaction mechanism of photocatalytic CH_4 oxidation on $\text{Au-CoO}_x/\text{TiO}_2$ using O_2 as the oxidant [128]

Copyright 2020, American Chemical Society. (b) Synthesis of A/R-TiO_2 and reaction mechanism of photocatalytic

conversion of CH₄ to HCHO on A/R-TiO₂ [134] Copyright 2022, American Chemical Society. (c) Photothermal-enhanced mechanism for selective oxidation of CH₄ to CH₃OH on CuS/TiO_{2-x} S-scheme heterojunction under full-spectrum irradiation [136] Copyright 2026, Elsevier.

Although the traditional Type-II heterojunction is conducive to charge separation, it will inevitably weaken the overall redox ability due to the migration of photogenerated carriers to bands with lower potentials. In contrast, the S-scheme heterojunction maintains the strongest redox potential through a unique charge transfer pathway [137]. Regarding the design of S-scheme heterojunction, Leng et al. constructed a CuS/TiO_{2-x} catalyst with full spectrum response [136]. The difference in the work function between the components produces a built-in electric field pointing to CuS (Figure 7c), which drives the electrons in the TiO_{2-x} conduction band to combine with the holes in the CuS valence band. This mechanism retains the highly oxidizing holes in TiO_{2-x}, which is conducive to methane conversion. Another advanced heterojunction mode is the MOF/semiconductor interface [138,139], which leverage the high specific surface area and adjustable pore environment of MOF to create a high-concentration microreaction space for CH₄ conversion. By modifying TiO₂ with ultra-small UiO-66-H crystallites, the concentration of active species on TiO₂ surface can be optimized by leveraging the porous MOF framework [140]. This strategy combines the adjustable microenvironment of MOF and the light capture ability of semiconductors, providing an effective way to accurately regulate the methane oxidation pathway and maintain high stability.

In summary, the construction of diverse heterostructures can accurately control the flow of photogenerated carriers and the redox potential of active sites, effectively inhibiting the excessive oxidation of methane. Future research should focus on the development of advanced composite systems with multi-functional interfaces. By integrating TiO₂ with novel components with specific functions such as spatial confinement, photothermal enhancement or radical stabilization, the synergy effect at the interface can be used to further improve the selectivity and yield of high-value products in practical applications. Table 5 summarizes the representative heterojunction-based TiO₂ photocatalysts and their methane conversion performances.

Table 5. Comparative summary of TiO₂-based heterojunction construction in photocatalytic methane conversion.

Catalyst	Reactants	Light Source	Products	Ref.
Au-CoO _x /TiO ₂	2.0 MPa CH ₄ , 0.1 MPa O ₂ , H ₂ O	300 W Xe lamp	2540 μmol g ⁻¹ h ⁻¹ (CH ₃ OH + CH ₃ OOH) 95% selectivity	[128]
Pt-CuO _x /TiO ₂	CH ₄ , O ₂ (atmospheric pressure, flow)	365 nm LED	C ₂ hydrocarbons 6.8 μmol h ⁻¹ , 60% selectivity	[129]
Ag-AgBr/TiO ₂	CH ₄ + air, 6 bar, flow	365 nm LED	C ₂ H ₆ 35.4 μmol h ⁻¹ , 79% selectivity (C ₂₊)	[130]
A/R-TiO ₂ (90% Anatase)	20 bar CH ₄ , 5 bar O ₂ , H ₂ O	300 W Xe lamp	HCHO 8.09 mmol g ⁻¹ h ⁻¹ , 97.4% selectivity	[134]
Au-Anatase/TiO ₂ (B)	CH ₄ (atmospheric pressure, flow)	300W Xe lamp	C ₂ H ₆ 170 μmol g ⁻¹ h ⁻¹ , 45% selectivity	[135]
CuS/TiO _{2-x}	1.5 bar CH ₄ , H ₂ O ₂	Simulated solar light	CH ₃ OH 3.68 mmol g ⁻¹ h ⁻¹ , 87.9% selectivity	[136]
UiO-66-H/TiO ₂	CH ₄ + air (atmospheric pressure)	UV-vis	Oxygenates 6454 μmol g ⁻¹ h ⁻¹ , 100% selectivity	[140]

Note: cross-comparisons between entries should be made with caution given the disparate reaction conditions.

4. Technical and Mechanistic Advancement for CH₄ Conversion

4.1. Innovation in Reactor Design

The Section 3 focuses on improving the catalyst design strategy of TiO₂-based photocatalyst, but the overall performance of photocatalytic methane conversion depends not only on the inherent characteristics of the catalyst, but also on the reactor configuration. Parameters such as light distribution, gas-liquid-solid mass transfer, methane/oxidant contact mode, and product removal can significantly affect the efficiency of methane conversion and product selectivity, especially for reaction systems that are highly sensitive to overoxidation. Therefore, catalyst design and reactor engineering should be considered more comprehensively.

In the gas-solid photocatalytic methane conversion system, the geometry of the reactor and the airflow mode are the key factors that determine the mass transfer efficiency. Early studies mainly use indium tin oxide (ITO) glass as the substrate; however, its flat surface limits the effective absorption of light. To address this, Lang et al.

proposed to modify Au/TiO₂ on ground glass with a diffuse reflective surface [100]. Their research results show that the inherent roughness of ground glass significantly enhances light capture and multiple reflection, leading to a 3.4-fold increase in C₂H₆ yield compared to smooth quartz. To further improve the uniformity and permeability of the catalyst layer, the follow-up research has turned to flexible porous substrates. Li et al. successfully deposited an Au nanocluster-loaded TiO₂ photocatalyst on the glass fiber membrane by vacuum filtration [101]. This method ensures the highly uniform distribution and excellent mechanical stability of the catalyst in the three-dimensional fiber network, and the methane conversion rate reaches 1.1 mmol h⁻¹. However, the reactor still adopts the conventional “flow-over” operation mode. The reactant mainly passed over the surface of the catalyst, so the deep catalytic site is still restricted by diffusion.

To overcome these diffusion barriers, Xiong et al. developed a customized 3D-printed reactor, which has multiple gas inlets (25 uniform inlet micropores) to realize a vertical “flow-through” mode of Au/TiO₂ photocatalyst fixed on the glass fiber membrane (Figure 8a) [141]. In this configuration, the mixed reaction gas is forced to pass through the catalyst layer on the glass fiber membrane, which significantly accelerates the diffusion of CH₄ molecules. Crucially, the micro-chamber design (about 5 mL) ensures that the generated C₂₊ product stays in the light-active area for an extremely short time, effectively suppressing excessive oxidation to generate CO₂. Thanks to this engineering synergy, the system achieved a remarkable conversion rate of 218.2 μmol h⁻¹ and 90% C₂ selectivity at high O₂ concentration (up to 6.8%).

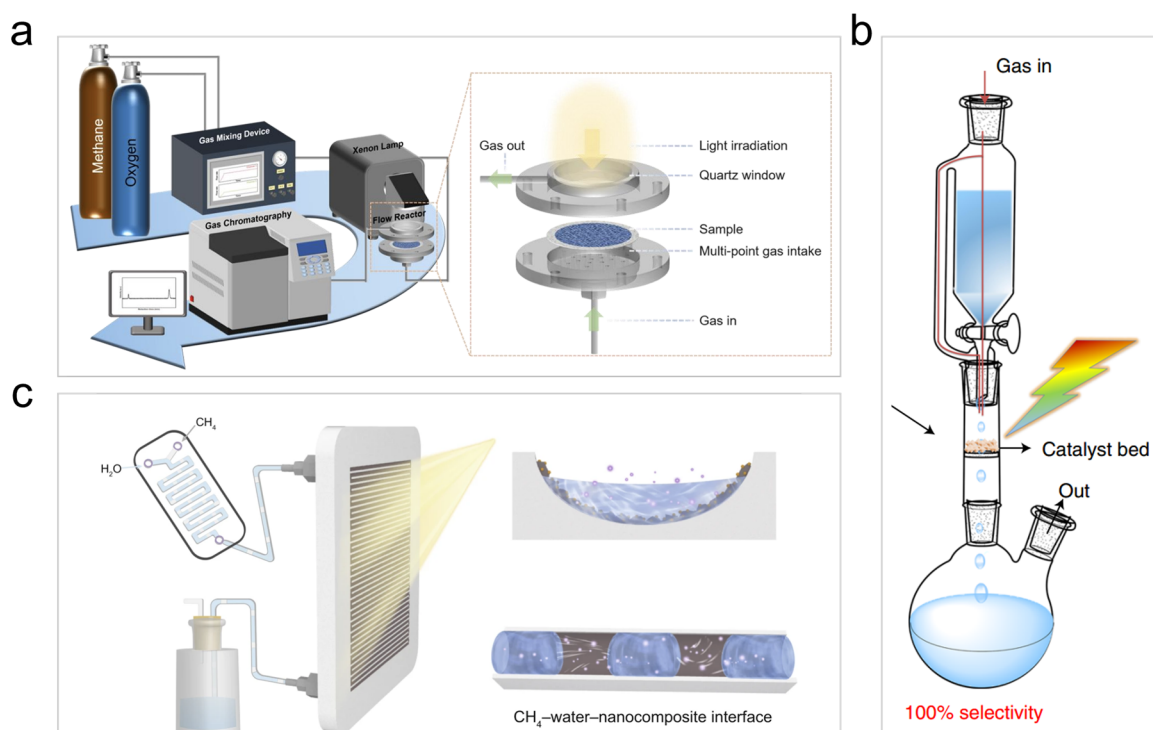


Figure 8. (a) Schematic diagram of the continuous flow reaction system and the multi-point gas intake flow reactor for photocatalytic OCM reaction [141] Copyright 2024, American Chemical Society. (b) View of the continuous-flow apparatus for photocatalytic conversion of CH₄ to CH₃OH [142] Copyright 2022, Springer Nature. (c) Schematic illustration of photochemical flow reaction device, including reactants supplier, homemade reactor and products collector [143] Copyright 2023, Springer Nature.

In the tri-phase (gas-liquid-solid) photocatalytic methane conversion system, the development of reactor design has been focusing on overcoming the physical bottleneck of extremely low solubility of methane in water. The traditional strategy mainly relies on high-pressure batch reactors, in which high-pressure CH₄ and O₂ (usually 5–30 bar) are introduced to increase their dissolved concentrations in the liquid phase. However, these conditions limit production efficiency and the possibility of continuous operation. In order to meet this challenge, researchers began to build an efficient gas-liquid-solid interface to enhance mass transfer and reaction kinetics. For example, An et al. reported a continuous-flow fixed-bed reactor, which adopts a dynamic tri-phase interface for PMOF-RuFe(OH), a porous metal–organic framework photocatalyst containing isolated mono-iron hydroxyl sites (Figure 8b) [142]. In the structure, the aqueous reactant solution is dripped slowly, and a thin liquid film is formed during the seepage

process, passing through the catalyst layer filled on the glass frit core. This allows gaseous methane to directly diffuse to the catalyst site wetted by the film, effectively bypassing the limitations of bulk water solubility.

Transition from a fixed-bed system to a dynamic suspension system, the use of a “pause-flow” microtube reactor has been proven to further enhance mass transfer and solve the issue of non-uniform illumination of a biphasic anatase/rutile TiO₂ photocatalyst [134]. By utilizing a T-type mixer, the catalyst suspension and the reaction gas are mixed to form a segmented gas-suspension flow, creating a high-density gas-liquid-solid contact interface in the channel. The toroidal vortices naturally generated in these discrete fluid segments ensure the full mixing of reactants and the timely removal of products, obtaining a significantly higher space-time yield than traditional batch reactors. In recent years, the concept of flow system has been further improved, and a synthetic strategy has been developed, which adopts PdO/Pd-WO₃ heterointerface nanocomposite photocatalyst fixed in the arc-shaped flow channel (Figure 8c) [143]. By fixing the catalyst on the inner wall of the reactor, the premixed bubbles and water phase are allowed to sweep over the active site. This design not only eliminates the require for catalyst recovery but also promotes the collision and coupling of *CH₃ and *CO intermediates through efficient tri-phase contact, realizing the highly selective continuous synthesis of CH₃COOH.

Overall, the above reactor configurations have been used in a variety of photocatalytic systems, including cocatalyst-modified TiO₂, phase-junction TiO₂, porous single-site photocatalysts, and heterointerface nanocomposites. These examples highlight the increasingly close interaction between catalyst design and reactor engineering in photocatalytic methane conversion. However, the systematic integration of these two aspects is still limited and needs to be further developed.

4.2. Advanced in-Situ Characterizations

In addition to reactor engineering, advanced in-situ characterization is also crucial for understanding how the above catalyst design strategies can improve the performance of methane conversion. In order to clarify the complex dynamic pathway of methane conversion, advanced in-situ characterization technology is widely used to identify short-lived active species and surface reaction intermediates. A comparative summary of representative in-situ characterization techniques, including their primary functions and advantages in photocatalytic methane conversion, is provided in Table 6. For example, in-situ electron paramagnetic resonance (EPR) is the cornerstone of detecting radical species. By employing specific spin-trapping agents (such as DMPO), the technology can sensitively capture key primary species generated by light excitation, such as transition metal ions in a paramagnetic valence state, •CH₃ and various ROS [144–147]. *In-situ* diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) can visualize the evolution process of surface-adsorbed intermediates in detail. By monitoring specific vibrational frequencies, researchers can track the formation of adsorbed methyl groups (*CH_x) resulting from methane dehydrogenation, the subsequent generation of methoxy species (*OCH₃), and the production of carbonyl (*CO) species under specific pathways in real time [148]. In the Fe-doped ZnO system [149], *in-situ* DRIFTS analysis reveals that Fe-doping passivates the activity of lattice oxygen and effectively weakens the interaction between *CH₃ and the surface. This regulation promotes the conversion of *CH₃O to *CH₃ intermediates instead of direct desorption, which is crucial to inhibit excessive oxidation. In-situ mass spectrometry (MS), especially synchrotron radiation photoionization mass spectrometry (SR-PIMS), has significant advantages in capturing gas-phase active species and evaluating catalytic kinetics [150,151]. Compared with the infrared spectroscopy limited to the surface adsorption state, in-situ MS can directly detect transient radicals (such as gas-phase •CH₃ and •OH), which are desorbed from the catalyst surface into the gas phase. The capability to detect these gas-phase intermediates makes it possible to quantitatively evaluate how radical desorption affects selectivity.

Understanding the generation, migration and recombination of photogenerated carriers is crucial for evaluating catalytic efficiency. Time-resolved Transient Absorption Spectroscopy (TAS) is a key technology for the study of carrier dynamics, which can monitor the evolution of the excited state on the time scale from femtosecond to microsecond [152,153]. By quantifying specific absorption characteristics, TAS can accurately evaluate the lifetimes of electrons and holes and their transfer rates. Transient absorption decay curves demonstrate that the interfacial internal electric field generated by the difference between the Pd and Co₃O₄ work functions drives the carrier directional migration and significantly extends the carrier lifetimes [154]. To further visualize the spatial distribution and driving force of charge separation, in-situ Kelvin Probe Force Microscopy (KPFM) provides critical experimental evidence. KPFM measures the contact potential difference (CPD) on the catalyst surface with a nanometer-scale spatial resolution, reflecting dynamic changes of the surface potential under illumination [155]. For example, KPFM imaging under dark and light conditions reveals a significant surface potential shift in Pt₁/ZnO single-atom catalysts [156], evidencing efficient hole enrichment at Pt sites. This spatial

charge separation suppresses recombination and maintains a high density of active centers for $\bullet\text{CH}_3$ generation, achieving excellent yield and selectivity.

To reveal the intrinsic active centers of the catalyst and its evolution on the atomic scale during the reaction process, in-situ surface and structural analysis techniques are indispensable. *In-situ* X-ray photoelectron spectroscopy (XPS) serves as a pivotal tool for monitoring surface valence states and charge transfer behaviors [157]. A heterojunction composed of ZnO and TiO_x shows a directional charge transfer through in-situ XPS characterization [158]. Under light irradiation, the Ti 2p binding energy shifts downward by 0.2 eV while the Zn 2p binding energy shifts upward by 0.2 eV, confirming the migration of electrons from ZnO to TiO_x . In addition, in-situ X-ray absorption spectroscopy (XAS) provides deep insights into the structural stability and local coordination of catalytic centers. Co K-edge XANES of $\text{Pd/Co}_3\text{O}_4$ identifies a distinct shift of the absorption edge toward lower energy under illumination and reaction atmospheres [154], which reflects the electron accumulation of the Co sites. At the same time, Pd K-edge EXAFS reveals an increase in Pd–C/O coordination intensity, which directly proves the interaction between Pd active sites and activated oxygen species or methane-derived intermediates in the photocatalysis process.

In general, advanced in-situ characterization technology constructs a coherent picture of photocatalytic methane conversion process by simultaneously tracking radical species, surface intermediates, and charge carrier dynamics. The integration of spectroscopy, microscopy and electron detection technologies enables a direct correlation between structural evolution and catalytic performance, laying the foundation for the design of catalysts with higher efficiency and selectivity.

Table 6. Comparative summary of in-situ characterizations for photocatalytic methane conversion.

<i>In-Situ</i> Characterization Techniques	Primary Functions	Advantage	Ref.
<i>In-situ</i> electron paramagnetic resonance (EPR)	Detection of short-lived radical species and paramagnetic ions	High sensitivity, Capturing photoexcited primary substances	[144–147]
<i>In-situ</i> diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS)	Monitoring the evolution of surface-adsorbed intermediates	Real-time visualization, Providing detailed reaction pathway insights	[148,149]
<i>In-situ</i> mass spectrometry (MS), synchrotron radiation photoionization mass spectrometry (SR-PIMS)	Detection of gaseous transient radicals and final products	Complementing IR	[150,151]
Time-resolved transient absorption spectroscopy (TAS)	Studying carrier dynamics	Femtosecond to microsecond time scales, Quantifying lifetimes and transfer rates	[152,153]
<i>In-situ</i> Kelvin Probe Force Microscopy (KPFM)	Visualizing surface potential variations and spatial charge distribution	Nano-scale resolution	[155,156]
<i>In-situ</i> X-ray photoelectron spectroscopy (XPS)	Monitoring surface valence states and charge transfer	Determination of the direction of directional charge migration	[157,158]
<i>In-situ</i> X-ray absorption spectroscopy (XAS)	Analyzing the oxidation state, local coordination, and structural stability of active centers	Providing atomic-scale structural information	[154]

5. Conclusions and Perspective

Photocatalytic methane conversion using TiO_2 -based materials has attracted increasing attention as a sustainable strategy to utilize abundant methane resources under mild conditions. As discussed in the review, significant efforts have been made to enhance the activity and selectivity of TiO_2 photocatalysts by means of facet engineering, doping and defect engineering, cocatalyst modification, porous structure construction, and heterojunction engineering. These modification strategies effectively regulate light absorption, charge-carrier separation, surface reaction kinetics, and intermediate conversion pathways, thereby significantly improving the photocatalytic methane conversion performance. In addition, the latest advances in reactor design and in-situ characterization technology have deepened our understanding of the reaction mechanism and catalyst evolution process, promoting the practical application of photocatalytic methane conversion systems.

Despite these advances, there are still some key challenges that limit the practical application of TiO_2 -based photocatalysts. First of all, pristine TiO_2 mainly responds to ultraviolet light due to wide band gap, which only accounts for a small fraction of the solar spectrum. Therefore, it is essential to extend the light-response range of TiO_2 to visible light or even the full spectrum in order to improve the conversion efficiency of solar energy. A variety of strategies, including plasmonic metal modification and dye sensitization, have shown great potential for enhancing visible light absorption. At the same time, rational control of charge transfer pathways and interfacial reaction kinetics under solar irradiation is still critical for achieving efficient methane activation.

Second, future research can go beyond the generation of traditional C₁ oxygenates and explore the direct coupling of methane conversion intermediates with organic molecules to produce higher-value multicarbon chemicals. Recent advances in photocatalytic coupling reactions show that surface-generated •CH₃ or oxygenated intermediates may participate in selective C–C bond formation. Therefore, the combination of methane activation and organic synthesis can provide new opportunities for the construction of long-chain hydrocarbons, alcohols, or other value-added compounds with higher economic value. To achieve this tandem transformation process, it is necessary to precisely regulate the generation and adsorption behavior of intermediates.

In addition, more attention should be paid to the actual methane emission scenarios. In many practical environments, such as coal mines, landfills, wastewater treatment plants, and agricultural emissions, methane usually exists in low concentrations rather than high concentrations. Efficient conversion of low-concentration methane into CO₂ or high-value chemicals remains challenging due to mass transfer restrictions. Therefore, future research should focus on the development of photocatalytic systems with enhanced methane adsorption capacity under dilute solution conditions, as well as reactor configurations suitable for continuous flow and large-scale operation. In addition, comprehensive techno-economic analysis and life-cycle assessment of photocatalytic methane conversion technology are crucial to assess its feasibility, energy efficiency and economic benefits.

Finally, computational and data-driven methods may provide an important opportunity to accelerate the discovery of high-efficiency TiO₂-based photocatalysts for methane conversion. Compared with the rapidly growing use of descriptor-based analysis and machine-learning-assisted catalyst design in photocatalytic CO₂ reduction [9,11,14], such strategies remain relatively underexplored in photocatalytic methane conversion. In future studies, key descriptors related to methane adsorption and activation, charge-carrier separation, oxygen vacancy formation, and the adsorption/desorption behavior of reaction intermediates (e.g., *CH₃, *OCH₃, and *CO) could be established to evaluate catalyst performance more systematically. Combined with high-throughput computation and machine-learning models, these descriptors may enable the rapid screening of dopants, cocatalysts, heterojunction components, and defect structures, thereby reducing empirical trial-and-error and guiding the rational design of TiO₂ photocatalysts with improved activity and selectivity.

Author Contributions

Z.L.: Conceptualization, data curation, formal analysis, writing—original draft preparation; H.S.: Data curation; W.Z.: Conceptualization, writing—review & editing, supervision, funding acquisition. All authors have read and agreed to the published version of the manuscript.

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Conflicts of Interest

The authors declare no conflict of interest.

Use of AI and AI-Assisted Technologies

No AI tools were utilized for this paper.

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