Review

Recent Advances in TiO$_2$-Based Photocatalysts for Reduction of CO$_2$ to Fuels

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Abstract: Titanium dioxide (TiO$_2$) has attracted increasing attention as a candidate for the photocatalytic reduction of carbon dioxide (CO$_2$) to convert anthropogenic CO$_2$ gas into fuels combined with storage of intermittent and renewable solar energy in forms of chemical bonds for closing the carbon cycle. However, pristine TiO$_2$ possesses a large band gap (3.2 eV), fast recombination of electrons and holes, and low selectivity for the photoreduction of CO$_2$. Recently, considerable progress has been made in the improvement of the performance of TiO$_2$ photocatalysts for CO$_2$ reduction. In this review, we first discuss the fundamentals of and challenges in CO$_2$ photoreduction on TiO$_2$-based catalysts. Next, the recently emerging progress and advances in TiO$_2$ nanostructured and hybrid materials for overcoming the mentioned obstacles to achieve high light-harvesting capability, improved adsorption and activation of CO$_2$, excellent photocatalytic activity, the ability to impede the recombination of electrons-holes pairs, and efficient suppression of hydrogen evolution are discussed. In addition, approaches and strategies for improvements in TiO$_2$-based photocatalysts and their working mechanisms are thoroughly summarized and analyzed. Lastly, the current challenges and prospects of CO$_2$ photocatalytic reactions on TiO$_2$-based catalysts are also presented.

Keywords: photocatalysis; carbon dioxide reduction; TiO$_2$-based photocatalysts; high efficiency
1. Introduction

Heavy dependence on fossil fuels since the past few centuries for industrialization and economic growth has depleted the sources of carbon-emitting fossil fuels and has led to record-breaking atmospheric concentrations of carbon dioxide (CO$_2$), which is a major component of greenhouse gases, thus contributing to global warming and climatic changes [1–3]. To mitigate the problematic impacts of CO$_2$ on human life and the environment, efforts have been made to reduce carbon emissions caused by capturing, storing, and transforming CO$_2$ into other valuable substances [4–6]. In addition, CO$_2$ is considered as one of the cheapest and most abundant carbon resources to produce various C$_1$ products such as carbon monoxide (CO), methane (CH$_4$), formic acid (HCOOH), and methanol (CH$_3$OH), which are critical for the synthesis of other value-added chemicals [7,8].

Lately, the electroreduction of CO$_2$ and photoreduction strategies have been paid increasing attention to as promising procedures to utilize CO$_2$ as a carbon building-block for synthesizing hydrocarbon fuels [9–11]. Electroreduction of CO$_2$ requires electricity as the driving force for the electrochemical reaction [12–15]. Therefore, the requirement of the energy input is concerning. This energy can be generated from non-renewable energy resources. Meanwhile, solar energy is among the most critical renewable energy sources along with wind energy, wave energy, and hydrogen energy [16]. Photoreduction systems activated by solar energy are a green but intermittent power source for catalyzing the reduction of CO$_2$. Such systems have been considered one of the most sustainable and cost-effective approaches to exploit solar energy combined with the utilization of anthropogenic CO$_2$ as a starting material of the carbon cycle to store energy in the form of chemical fuels [8,17,18].

Titanium dioxide (TiO$_2$) has been the benchmark for photocatalytic studies over nearly four decades since the seminal work by Fujishima and Honda, who showed the high photochemical stability, low-cost features, facile preparation, abundance, and low toxicity of TiO$_2$ [19]. TiO$_2$ exhibits the most extensive applications as a semiconductor and can be used in a wide range of photocatalysis applications including water splitting, photodegradation of pollutants, dye bleaching, and water desalination, thus contributing to solving the environmental and energy crisis [20–27]. Parallel to water splitting technologies, an extensive line of studies on TiO$_2$-based photocatalysts for CO$_2$ reduction has been conducted to overcome obstacles including limited light-harvesting, charge separation hindering improved process efficiencies, inefficient selectivity of products, the inability to suppress the competing the hydrogen evolution reaction (HER), and catalytic instability [28–31]. In this study, we therefore review the photocatalytic conversion of CO$_2$ to fuels using the recently advanced TiO$_2$-based materials. The fundamentals of CO$_2$ photoreduction are discussed to understand the factors affecting the performance of photocatalysts, and the updated progress in the enhancement of its efficiency is comprehensively discussed. The effective strategies for overcoming the limitations of TiO$_2$-based photocatalysts are categorized as follows: (i) Design of nanostructured TiO$_2$-based catalysts, (ii) modification of TiO$_2$ facial properties, and (iii) cocatalysts for TiO$_2$ photocatalysts. Lastly, the current challenges and directions for future progress are provided, which could offer guidelines for the future development of CO$_2$ reduction on TiO$_2$-based photocatalysts.

2. Fundamentals of CO$_2$ Photocatalytic Reduction

Thermodynamically, CO$_2$ is one of the most stable linear molecules, showing the highest oxidation state of the carbon atom with a Gibbs free energy of $\Delta G^0 = -394.4$ kJ mol$^{-1}$. A high input energy is required to activate the CO$_2$ molecule, following the equation:

$$\Delta G^0 = nFE^0.$$  (1)
In reality, however, to break the C=O bond and bend the linear geometry of CO₂, a more negative potential than E° is required to make the ΔG° value negative enough to spontaneously accelerate the conversion of CO₂ and to compensate for the overpotential (Equation (2)):

$$E = \eta + E^o$$

(2)

where ΔG° is the standard Gibbs free energy, E is the required potential, E° is the standard potential, η is the overpotential, n is the number of transferred electrons, and F is the Faraday constant.

In addition, the presence of reductants providing protons to react with the adsorbed CO₂ on a photocatalyst surface and electrons to form products assists the process of CO₂ conversion by lowering the required input energy in comparison to the absence of reducing agents, in which the reduction of CO₂ proceeds by a photocatalyst alone and is much more difficult because of the high stability of inert CO₂. Therefore, photoreduction of CO₂ is commonly conducted with a reductant, such as H₂ or/and H₂O, making the conversion of CO₂ into fuels more feasible and more efficient from the view point of consumed energy [32,33]. In a CO₂(g)/H₂O(g/L) or CO₂(g)/H₂(g) system, photoexcited electrons are generated under light irradiation and are transferred, and then they react with the adsorbed CO₂ on the photocatalyst surface along with protons provided by the reducing agents to yield the reduced products. H₂O (vapor or liquid) is well known as an inexpensive and safer reductant than H₂ gas which is dangerous, although HER is also coupled in the H₂O phase, which lowers the CO₂ reduction efficiency because of their similar potentials for generating intermediates. Various products from the CO₂ reduction reaction combined with the competing HER and their standard potentials are presented in Table 1.

| Product          | Reaction                                      | n  | E° (V vs. NHE) |
|------------------|-----------------------------------------------|----|----------------|
| Carbon monoxide  | CO₂ + 2H⁺ + 2e⁻→CO + H₂O                    | 2  | -0.51          |
| Formic acid      | CO₂ + 2H⁺ + 2e⁻→HCOOH                        | 2  | -0.58          |
| Oxalate          | 2CO₂ + 2H⁺ + 2e⁻→H₂C₂O₄                      | 2  | -0.87          |
| Methanol         | CO₂ + 6H⁺ + 6e⁻→CH₃OH + H₂O                  | 6  | -0.39          |
| Methane          | CO₂ + 8H⁺ + 8e⁻→CH₄ + 2H₂O                   | 8  | -0.24          |
| Ethanol          | 2CO₂ + 12H⁺ + 12e⁻→C₂H₂O₂H + 3H₂O           | 12 | -0.33          |
| Ethane           | 2CO₂ + 14H⁺ + 14e⁻→C₂H₆ + 4H₂O               | 14 | -0.27          |
| Hydrogen         | H₂O + 2e⁻→2OH⁻ + H₂                          | 2  | -0.41          |

Importantly, the formation of unstable radical anion CO₂⁻ has been proved to be the most widely recognized mechanism to activate CO₂ molecules in the initial stage of the photoreduction process. However, this activation requires a very negative equilibrium potential of −1.49 V vs. reversible hydrogen electrode (RHE) at pH = 7 to form the CO₂⁻ intermediate, resulting in a significant increase in the required negative potential applied for electrochemical reduction of CO₂ compared with the standard potentials in Table 1.

The overall principles of the photoreduction CO₂/H₂O(g/L) system are illustrated in Figure 1. Under light irradiation, incident photons with an equal or higher energy than that of the bandgap semiconductor (e.g., 3.2 eV for anatase TiO₂), which act as the photocatalyst, are absorbed and the pair-charges, electrons and holes, are generated. This is followed by the separate transportation of the generated electrons and holes to the photocatalyst surface. Subsequently, the photogenerated electrons reduce CO₂ to value-added chemicals (step number 1) while water is oxidized by holes to oxygen molecules (step number 2). The recombination of the electron-hole pairs, which may consume a lot amount of photogenerated charges, in the bulk and on the surface can occur in step numbers 3 and 4, respectively. Proton reduction, which is called HER, appears to be spontaneous in step number 1 under aqueous conditions and competes with the reduction of CO₂.
Figure 1. Schematic illustration of photoreduction of CO$_2$ into fuels on TiO$_2$-based photocatalysts.

For the selection of the photocatalyst material, the conductive band (CB) and valence band (VB) positions of semiconductors are critical factors, which help analyze the possibility for the redox reaction. Alternative semiconductors possess different CB and VB positions, thus varying the band gap, which is the potential energy between the CB and VB (Figure 2a) [34–40]. Theoretically, for instance, anatase TiO$_2$ with CB and VB potentials of $-0.5$ eV and $2.7$ eV, respectively, enables the reduction of CO$_2$ into several fuels (such as CH$_4$, CH$_3$OH, and CO) and oxidizes H$_2$O because its CB is more negative than the reduction potential to form products, whereas its VB more positive than the redox potential of the reductant. Nonetheless, the high band gap (3.2 eV) requires a high energy of photons with a short wavelength (UV light) to activate photoexcitation.

Figure 2. Cont.
which will be discussed in the following sections. play a significant role on specifying the surface adsorption properties and surface electronic structures, 3.1. Nanostructured TiO\textsubscript{2} Design

The TiO\textsubscript{2} possesses three types of crystal phases: Anatase, rutile, and brookite. The first two crystal structures are usually used as photocatalysts. The photocatalytic activity can be improved by creating a mixture of different crystal structures rather than using a single crystal phase due to the improved charge separation and transfer efficiency induced by heterojunction effects [44–46]. To this end, Chai et al. controlled the composition of anatase and rutile phases in TiO\textsubscript{2} to enhance the photoactivity by simply varying the annealing temperature [47]. As expected, TiO\textsubscript{2} nanoparticles (NPs) were composed of both anatase and rutile crystal phases, leading to an increase in the electron-hole separation caused by the created heterojunction (Figure 3a,b). They also found that the optimal fraction of phase content for their TiO\textsubscript{2} photocatalyst was 17.5\% rutile phase. Moreover, another factor that contributes to the catalytic activity is morphology. A synergistic influence of crystal phase content and morphology can be expected to improve photocatalytic performance. To elucidate this hypothesis, 1-D hierarchical mesoporous TiO\textsubscript{2} nanofibers were synthesized using combined electrospinning and sol-gel methods. Insights into the interaction of adsorbed CO\textsubscript{2} with the semiconductor surface are important because the structure and composition of the catalytic sites can significantly vary the pathways and selectivity of different products. Thus, Curtiss et al. proposed diverse binding configurations of activated CO\textsubscript{2} molecules on the TiO\textsubscript{2} surfaces (Figure 2b) [41]. They also found that the cation sites on the Ti surface can lower the reaction barrier to activate CO\textsubscript{2} and the stability of CO\textsubscript{2}– intermediates to enhance CO\textsubscript{2} photoreduction.

Briefly, the photoreduction of CO\textsubscript{2} on TiO\textsubscript{2} can encounter some intrinsic challenges such as the low light-harvesting efficiency, charge recombination, thermodynamic difficulty in activation of CO\textsubscript{2}, the required high negative overpotential for intermediates, the wide distribution of products from CO\textsubscript{2} reduction in kinetics, and the competition of the favorable HER from H\textsubscript{2}O reduction. These limitations could be overcome to enhance the photocatalytic activity of CO\textsubscript{2} on TiO\textsubscript{2}-based photocatalysts by focusing on some critical factors including surface molecular structures and charge transfer behaviors, which will be discussed in the following sections.

3. Advances in TiO\textsubscript{2}-Based Photocatalysts for CO\textsubscript{2} Reduction

3.1. Nanostructured TiO\textsubscript{2} Design

Various nanostructured TiO\textsubscript{2}-based photocatalysts with different surface molecular structures play a significant role on specifying the surface adsorption properties and surface electronic structures, and thus, the photocatalytic activity of a photocatalyst is determined by its electronic structure resulted from the light absorption efficiency and redox potential of the excited charges. In addition, the surface charge transfer configurations also contribute to the photocatalytic activity by accelerating electron and hole transportation and impeding electron-hole recombination [42,43]. To that end, many studies have reported advances for CO\textsubscript{2} photoreduction on engineering of crystal phases [44–48], facets [41,49–57], and TiO\textsubscript{2}-dispersed on porous materials [58–61].

3.1.1. Crystal Phases

TiO\textsubscript{2} possesses three types of crystal phases: Anatase, rutile, and brookite. The first two crystal structures are usually used as photocatalysts. The photocatalytic activity can be improved by creating a mixture of different crystal structures rather than using a single crystal phase due to the improved charge separation and transfer efficiency induced by heterojunction effects [44–46]. To this end, Chai et al. controlled the composition of anatase and rutile phases in TiO\textsubscript{2} to enhance the photoactivity by simply varying the annealing temperature [47]. As expected, TiO\textsubscript{2} nanoparticles (NPs) were composed of both anatase and rutile crystal phases, leading to an increase in the electron-hole separation caused by the created heterojunction (Figure 3a,b). They also found that the optimal fraction of phase content for their TiO\textsubscript{2} photocatalyst was 17.5\% rutile phase. Moreover, another factor that contributes to the catalytic activity is morphology. A synergistic influence of crystal phase content and morphology can be expected to improve photocatalytic performance. To elucidate this hypothesis, 1-D hierarchical mesoporous TiO\textsubscript{2} nanofibers were synthesized using combined electrospinning and sol-gel methods.

Figure 2. (a) conductive band (CB), valence band (VB), and bandgap energies of several semiconductors summarized from the references [34–40]. Reproduced with permission from [34]. Copyright 2015, Royal Society of Chemistry. (b) Configurations of CO\textsubscript{2} molecule on TiO\textsubscript{2} surface. Reproduced with permission from [41]. Copyright 2012, American Chemical Society.
The obtained photocatalyst exhibited higher activity than TiO$_2$ NPs prepared only by the sol-gel procedure [48]. The fast charge transport and impeded electron-hole recombination caused by the nanofiber morphology led to improved activity. Meanwhile, the 1-D fiber photocatalyst with a higher ratio of rutile to anatase phases (20:80) produced four and 2.5 times higher H$_2$ and CO, respectively, than the counterpart containing a lower ratio of rutile to anatase phase (7:93), revealing the crucial role of crystalline phase composition in photocatalytic activity.

3.1.2. Effect of Facets

Facet engineering of TiO$_2$ photocatalysts, which is another promising strategy to achieve high photocatalytic activity via CO$_2$ adsorption on the catalyst surface, photoinduced activation, and charge separation, has been extensively studied [41,49–55]. In general, the {101} facet is more thermodynamically stable than {001} facets, suggesting that anatase TiO$_2$ crystals usually possess the dominant exposed {101} facets [49]. Using first-principle calculations, Curtiss et al. investigated the binding configuration of intermediates on anatase {101} surfaces and found that the reduced {101} anatase surfaces favor CO$_2$ binding along with charge transfer to CO$_2$ [41,50]. As a result, the adsorption of CO$_2$ and the charge transfer from the surface of anatase TiO$_2$ photocatalysts to CO$_2$ was theoretically demonstrated to be enhanced on the preferentially exposed {101} facets. Nevertheless, Han et al. unveiled that {001} facets are more reactive in photocatalytic reduction of CO$_2$ than the low-energy {101} surfaces because of the high density of active unsaturated Ti atoms and active surface oxygen atoms [51]. Therefore, the coexposed facet approach is believed to promote spatial charge separation and form a facet-related heterojunction, thus resulting in longer charge carrier lifetimes, which can hinder electron-hole recombination and accelerate electron and hole transportation while maintaining the high adsorption of CO$_2$. In a subsequent study, Yu et al. appropriately manipulated the efficient ratio of coexposed {101} and {001} facets to synergistically leverage the CO$_2$ adsorption and reactivity on both facets [52]. By varying the HF amount used during the synthesis of TiO$_2$ nanosheets, the growth of the {101} and {001} facets can be adjusted. Therein, the optimal HF amount used is

Figure 3. (a) Heterojunctions induced from rutile and anatase crystal phases of TiO$_2$. (b) TEM images of anatase [101] and rutile phases [110]. (a,b) Reproduced with permission [47]. Copyright 2016, Royal Society of Chemistry. (c) Schematic illustration of the spatial separation of redox sites on TiO$_2$ prepared by alternating HF amounts. (d) Comparison of the CH$_4$ production rate of P25 and the TiO$_2$ samples prepared by varying HF amounts. (c,d) Reproduced with permission [52]. Copyright 2014, American Chemical Society. (e) Transformation of the anatase phase of TiO$_2$ nanotubes into the rutile phase with [110] as the dominant plane using the flame annealing method. (e) Reproduced with permission [56]. Copyright 2019, Elsevier.
4.5 mL to obtain the {001} and {101} exposed facets in a proportion of 55:45, with a CH₄ yield from photoreduction of CO₂ of 1.35 μmol g⁻¹ h⁻¹ (Figure 3c,d).

Nonetheless, Kar et al. very recently reported an efficient method to transform anatase phase TiO₂ nanotubes into the rutile phase with the [110] facet as the dominant plane using the flame annealing method (Figure 3e) [56]. Flame-annealed nanotubes prepared in a water-based electrolyte (FANT-aq) exhibited superior yield (156.5 μmol g⁻¹ h⁻¹) in the presence of the rutile phase as the only crystalline phase. High activity of the FANT-aq can be attributed to the increased visible-light absorption due to the reduced band gap induced by the pure rutile phase, defects and sub-energy levels, square morphology, and the preferentially oriented rutile [110] facet.

Remarkably, Yang et al. lately prepared hydrogenated nanotube/nanowire photocatalysts assembled from TiO₂ nanoflakes with an exposed clean {111} facet, which is believed to be the origin of the enhanced solar absorption and the good charge separation to attain a superior photocatalytic performance up to 1708.1 μmol g⁻¹ h⁻¹ CH₄ at 373 K under the irradiation of a 300-W Xe lamp, which is one of the best performances for methane production. Importantly, a spontaneous electric field (Es) is demonstrated to exist between the polar TiO₂ {111} and {111} planes, under which photoinduced electrons and holes migrate to the positive Ti–TiO₂ {111} and negative O–TiO₂ {111} polar surfaces, respectively, which is followed by the subsequent redox reactions to reduce CO₂ into CH₄, as shown in Figure 4 [57].

![Figure 4](image-url)  
**Figure 4.** (a) SEM and (b) TEM images of the catalyst prepared in the TOBT-CH₃COOH-H₂O-H₂SO₄ system. (c) HRTEM image and (d) the corresponding FFT pattern from the box in (b). (e) Structural illustration of the TiO₂ nanotubes/nanowires constructed with nanoflakes with exposed [111] crystal facets. (f) The schematic illustrations of charge separation under Es and photocatalytic reaction. (g) Photocatalytic CO₂ reduction activity and stability in recycling the photocatalyst. (a–g) Reproduced with permission [57]. Copyright 2019, Royal Society of Chemistry.

3.1.3. Well-Dispersed TiO₂ on Porous Materials

Porous materials have been utilized as a supporter for catalysts because of their high surface area, well-dispersed active sites, large adsorption capacities, and alternative pore sizes suitable for facile diffusion and transportation of gas and liquid reactants. Therefore, porous materials including zeolite and hierarchical silica have been considered as potential supporting candidates in photocatalytic reduction of CO₂. As one of the earliest investigations, in a study by Anpo et al., highly dispersed TiO₂ on zeolites (Ti-MCM) were synthesized by a hydrothermal method for photoreduction of CO₂ to CH₄ and CH₃OH [58–60]. The well-dispersed Ti zeolites catalyzed the photoreduction of CO₂
into CH₄ and exhibited approximately 10-fold higher photocatalytic efficiency than TiO₂ powder. Interestingly, high activity for CH₃OH formation was achieved on Ti-MCM-48, whereas the bulk TiO₂ counterpart only produced CH₄ as the product. The results indicate that the 3-D channel structure of zeolites in Ti-MCM-48 is not only beneficial for the high dispersion of TiO₂, but is also beneficial for the high amount of adsorbed CO₂ and production of CH₃OH. It is plausible that the formation of charge transfers excited complexes (Ti³⁺-O⁻)⁺ on the isolated TiO₂ species in zeolites. Moreover, OH-radicals are formed from the decomposition of H₂O, which react with methyl from reduction of CO₂ and finally generate CH₃OH [59]. In a subsequent study, Ti-SBA-15 synthesized with a higher pore size exhibited 106 μmol CH₄ g⁻¹ h⁻¹ production via photoreduction of CO₂ into CH₄ and CH₃OH under UV irradiation. This activity is 20 times higher than that of Ti-MCM-41 and Ti-MCM-48 [61].

3.2. Modification on TiO₂ Surface

Surface modifications of the crystal structure can act as active sites on metals and/or metal-oxide catalysts, modifying the electronic structure and binding strength of intermediates, and thus, influencing the catalytic activity. Two popular approaches on TiO₂-based photocatalyst surface are related to oxygen vacancies [62–72] and basic-site functionalized modifications [73–78].

3.2.1. Oxygen Vacancies

Oxygen defects are one of the most famous and efficient approaches to enhance photocatalytic activities [62,63]. The behavior of CO₂ adsorbed on oxygen defects (Vₒ) on the TiO₂ [110] surface was investigated by Lee et al. [64] Their results unveiled that with the existence of Vₒ, one oxygen atom of CO₂ can be situated at the position of the oxygen defect and can the CO₂ molecule on TiO₂ with a bridge formed by the adsorption of the oxygen atom from CO₂, which can enhance CO₂ trapping and lower the activation barrier (Figure 5a,b). Recently, Alexandrova et al. employed density functional theory calculations to systematically study the role of oxygen vacancies on anatase TiO₂ [101] surface (Figure 5c–e) [65].

The significance of oxygen vacancies on defected TiO₂ has been ascertained in the enhancement of CO₂ adsorption, activation, dissolution, and stabilization of reaction intermediates. Li et al. found that the photocatalytic activity of the enriched oxygen defect on TiO₂ nanocrystals could be increased compared with that on unmodified crystals [66]. By controlling coexposed [001] and [101] facets, the highest performance was observed on TiO₂-x[001]-[101] with a CO production rate of 55 and 27 μmol g⁻¹ h⁻¹ (quantum yield of 0.31 and 0.134%) under UV-VIS and visible light, respectively (Figure 6a). This excellent performance, even under visible light, can be attributed to the high CO₂ adsorption capacity, combination of [001] and [101] facets, and the new energy state of Ti³⁺ cations, which improve the activation and conversion kinetics of the adsorbed species. Later, a facile hydrothermal method was reported to synthesize TiO₂ with a high concentration of Ti³⁺ [67]. Because of the oxygen vacancies and coexposed [001] and [101] facets, the photocatalytic activity was improved with wide-spectrum solar light absorption to enhance CO₂ photoconversion and CH₄ selectivity under sunlight irradiation.

Oxygen vacancies in TiO₂ can also be formed from the introduction of other elements to achieve high efficiencies under visible light. This is because the formation of Ti³⁺ caused by oxygen deficiency creates an intermediate band and thus accelerates electron-hole pair separation. In addition, the oxygen vacancy sites on the surface of the photocatalysts could allow adsorption of more CO₂ compared with the bulk surface [62,68–72]. Ye et al. prepared an oxygen-deficient perovskite structure of self-doped SrTiO₃-x for CO₂ photoreduction under visible light [62]. Using a one-step combustion method followed by calcination in Ar at temperatures ranging from 1200 to 1400 °C, oxygen vacancies were generated coupled with Ti³⁺ to activate visible-light absorption. The increase in oxygen vacancies was found to be positively correlated with the CO₂ chemical adsorption capacitance. The optimized SrTiO₂₈₂₃ photocatalysts showed the highest conversion of CO₂ in photoreduction to CH₄ with a quantum efficiency of 0.21% at 600 nm. Analogously, for the first time, Li et al. reported the spontaneous dissolution of CO₂ into CO even in the dark on a defective and partially oxygen-depleted Cu(I)/TiO₂-x
surface [68]. The photocatalyst was prepared by thermal annealing of Cu(OH)$_2$/TiO$_2$ in an inert environment at moderate temperatures to generate surface oxygen vacancies due to partial oxygen loss and the reduction of Cu$^{2+}$ to Cu$^+$ (Figure 6b). Moreover, the oxidation state of copper on TiO$_2$ induced by the pretreatment conditions can play an important role in the photoreduction performance of catalysts. The active charge separation of H$_2$-pretreated Cu/TiO$_2$ can be attributed to the synergistic effect of the mixture of Cu$^+$ and Cu and the oxygen vacancy defects [69]. In addition, metallic Cu particles have been reported to promote the formation of oxygen vacancies in black TiO$_2$-coated Cu NPs through metal-oxide interactions, thus improving the visible-light adsorption and the adsorption of CO$_2$ to improve photocatalytic activity [70]. Furthermore, oxygen vacancies are also formed from the introduction of co-dopants [71]. Lee et al. reported high production yields of CH$_4$ and CO under visible light, which are 933 and 588 μmol g$^{-1}$ h$^{-1}$, respectively, on 2Cu@4V-TiO$_2$/PU (PU = polyurethane) [72].

**Figure 5.** (a) Schematic representation showing V$_o$, OH$_b$, and CO$_2$ molecule adsorbed at a V$_o$ site on reduced TiO$_2$. (b) Scanning Tunneling Microscope (STM) image of the TiO$_2$ [110] surface after adsorption of CO$_2$ at 55 K. (a,b) Reproduced with permission from [64]. Copyright 2011, American Chemical Society. (c–e) Configurations of adsorbed CO$_2$ on O$_v$ site: (c) CO$_2$(H); (d) CO$_2$(V); (e): Adsorption and dissociation of CO$_2$ on the oxygen vacancy site. The Ti, O, and O in CO$_2$ and C are shown in silver, red, pink, and gray colors, respectively. (c–e) Reproduced with permission from [65]. Copyright 2019, American Chemical Society.
passivation of TiO\textsubscript{2} promote the chemisorption and activation of photocatalysts. Ye et al. modified the TiO\textsubscript{2} surface by alcoholysis method \cite{78}. As a result, the conversion of CO\textsubscript{2} nanosheet-based yolk@shell microspheres using one-pot diethylenetriamine mediated anhydrous harvesting ability and improved CO\textsubscript{2} to improve CO\textsubscript{2} can be ascribed to the increased concentration of surface Ti\textsuperscript{4+} compared with pristine porous-TiO\textsubscript{2} layers from 1 to 100 and found that five layers of MgO exhibited 4- and 21-fold higher CO production 

anatase-rutile phases by atomic layer deposition (ALD) \cite{76}. They increased the number of atomic MgO layers on porous TiO\textsubscript{2}. \cite{76}. 

\textbf{Figure 6.} (a) Generation of CO on oxygen-deficient blue TiO\textsubscript{2} nanocrystals with coexposed [101]-[001] facets in comparison with some other photocatalysts. Reproduced with permission from \cite{66}. Copyright 2016, American Chemical Society. (b) A rational mechanism for spontaneous dissociation of CO\textsubscript{2} on a defective Cu(I)/TiO\textsubscript{2-x} catalyst even in the dark. Reproduced with permission from \cite{68}. Copyright 2012, American Chemical Society. (c,d) TEM images of deposition of five atomic layers of MgO on porous TiO\textsubscript{2}. (e) CO production rate of different atomic layer deposited MgO surface coating layers on porous TiO\textsubscript{2}. (c-e) Reproduced with permission from \cite{76}. Copyright 2018, Elsevier.

3.2.2. Surfaces of Basic Functional Sites

Because CO\textsubscript{2} molecules can act as an electron acceptor because of the electrophilic carbon atom, some studies have explored the utilization of basic hydroxides, oxides, and amine functional groups to promote the chemisorption and activation of photocatalysts. Ye et al. modified the TiO\textsubscript{2} surface by loading 3 wt\% solid NaOH to obtain 52 \textmu mol g\textsuperscript{-1} CH\textsubscript{4} within 6 h; in contrast, bare TiO\textsubscript{2} did not show any CH\textsubscript{4}-production activity \cite{73}. Similarly, Wang et al. loaded MgO onto the TiO\textsubscript{2} surface to transform CO\textsubscript{2} into CO via photoreduction with H\textsubscript{2}O vapor \cite{74}. The introduction of MgO into Pt-TiO\textsubscript{2} can generate 2.2 \textmu mol of CH\textsubscript{4} within 10 h \cite{75}. Lately, Li et al. coated an ultrathin MgO layer on porous TiO\textsubscript{2} mixed anatase-rutile phases by atomic layer deposition (ALD) \cite{76}. They increased the number of atomic MgO layers from 1 to 100 and found that five layers of MgO exhibited 4- and 21-fold higher CO production compared with pristine porous-TiO\textsubscript{2} and common P25, respectively (Figure 6c-e). The enhanced activity can be ascribed to the increased concentration of surface Ti\textsuperscript{3+} species and hydroxyl groups caused by the uniform dispersion of MgO layers, which act as active sites for adsorption and photoreduction of CO\textsubscript{2}. Furthermore, the deposited MgO layers promoted electron-hole separation because of the passivation of TiO\textsubscript{2} states on the surface. Likewise, amine-functionalized TiO\textsubscript{2} was synthesized using monoethanolamine (MEA) to improve CO\textsubscript{2} adsorption, thus enhancing the photocatalytic activity by approximately three times than the pristine TiO\textsubscript{2} \cite{77}. Liu et al. also reported the high visible-light harvesting ability and improved CO\textsubscript{2} adsorption capacity of hierarchical amine-functionalized titanate nanosheet-based yolk@shell microspheres using one-pot diethylenetriamine mediated anhydrous alcoholyis method \cite{78}. As a result, the conversion of CO\textsubscript{2} exhibited a CH\textsubscript{3}OH yield of 8 \textmu mol g\textsuperscript{-1} h\textsuperscript{-1} under visible-light irradiation.
3.3. Cocatalysts

The introduction of cocatalysts into TiO$_2$ photocatalysts can be beneficial for CO$_2$ reduction not only by enhancing the charge transfer via formation of a heterojunction, thus improving the charge carrier separation, but also by forming supplementary active sites for the reaction to increase the adsorption of CO$_2$ and stabilization of intermediates in the photoreaction [79–82].

3.3.1. Metal and Metal-Oxide Cocatalysts

Metals and metal oxides have been frequently employed as cocatalysts with TiO$_2$ to improve the performance of TiO$_2$ [35,75,81–96].

When a cocatalyst system is illuminated, a transfer of photoinduced electrons from TiO$_2$ to the metallic surface possessing a larger work function at the interface can occur, and thus, metallic sites can act as an electron-sink to activate CO$_2$ and generate the bent CO$_2^-$ intermediate [6,80]. Wang et al. reported the effect of noble metal cocatalysts on the photocatalytic activity of TiO$_2$ and found that the rate of CH$_4$ formation increased as follows: Ag < Rh < Au < Pd < Pt. This result agrees well with the increase in the charged-pair separation efficiency [75]. Pd NPs on the surface of TiO$_2$ have also been reported to act as sites for the adsorption and activation of CO$_2$ [82].

In addition, the size of metallic NPs is a crucial factor determining the activity and CH$_4$-formation rate. The optimum size of Pt NPs on 1-D nanostructured TiO$_2$ single crystals to produce CH$_4$ at an excellent rate of 1361 µmol g$^{-1}$ h$^{-1}$ was found to be 1.04 ± 0.08 nm; the result was associated with a quantum yield of 2.41%, which is advanced compared with the production by pristine TiO$_2$ and P25 catalysts [35]. The energy level of the small Pt coated on 1-D TiO$_2$ was rationally positioned at a higher level than the CB edge of TiO$_2$, impeding photoinduced electron transfer (Figure 7a), which is beneficial for CO$_2$RR. Recently, Liu et al. synthesized ultrafine 1.1-nm Pt nanoparticles photoreduced and highly dispersed on ultrathin TiO$_2$ fabricated by deprotonated ethylene glycol as a support (P-Pt/TiO$_2$-U) [83]. The synergistic effects from both ultrathin TiO$_2$ and ultrafine highly dispersed Pt are as follows: Increased electron rate transfer on ultrathin TiO$_2$ nanosheets with abundant defects and ultra-large surface area, the facilitated separation of photogenerated electron-hole pairs induced by ultrafine Pt NPs, which was proved to improve the light-harvesting capacity and quantum efficiency, and finally, the improved adsorption ability of CO$_2$ caused by the synergy of metal and support (Figure 7b,c).

As mentioned above, Cu is a popularly used transition metal for cocatalysts of TiO$_2$. Numerous studies have assessed its contribution to cocatalyst systems. Cu-moieties decorated on the surface of N-doped TiO$_2$ nanotubes and Cu on TiO$_2$-SiO$_2$ catalysts have demonstrated improved CH$_4$ formation from CO$_2$RR. Interestingly, Corma et al. reported the conversion of CO$_2$ to formic acid with a yield of 25.7 µmol g$^{-1}$ h$^{-1}$ on Cu-doped TiO$_2$ under UV-rich illumination with Na$_2$S [84]. CuO-TiO$_2$ hollow microspheres with CuO extensively dispersed on the shell have been reported to improve the light-harvesting efficiency to produce CO and CH$_4$ from photoreduction of CO$_2$ under UV conditions [85]. This result can be attributed to the improved electron trapping ability induced by CuO. Meanwhile, hydrogenated hollow microspheres, in which Cu$^{2+}$ was reduced to Cu$^0$, could further enhance CH$_4$ production because of the hole capturing caused by Cu$^0$ and H$_2$ formation from water dissociation for CH$_4$ evolution. Recently, Jiang and co-workers employed atomically dispersed Cu supported on ultrathin TiO$_2$ nanosheets to photocatalytically reduce CO$_2$ to CO [86]. Most importantly, Cu is an abundant, non-toxic, and low-cost metal, which is a potential alternative to noble metals. In this study, a method is also presented to recycle the catalyst for long-term utilization. Similarly, Cu was recently ascertained to suppress the hydrogen evolution in CO$_2$ photoreduction on Cu-TiO$_2$ to selectively produce CO at a high rate [81].
was created on TiO₂ photocatalyst using hydrous hydrazine Au–Cu bimetal as the cocatalyst supported on SrTiO₃/TiO₂ nanostructured design for further enhancement of the rate in the future.

approaches to achieve a high production rate for photoreduction of CO₂, shedding light on the hybrid approach to mitigate the problematic CO₂ gas. This research can be a representative study that manipulated various aspects of photocatalytic CO₂ reduction.

Furthermore, the employment of binary cocatalysts was investigated on Cu₂O/Pt/TiO₂ and MgO-Pt/TiO₂ systems [75,87]. The introduction of Pt on TiO₂ was demonstrated to promote the capture of photogenerated electrons and to hinder pair-charge recombination; however, H₂ evolution was spontaneously increased. To suppress H₂ generation and enhance the chemisorption and activation of CO₂, Cu₂O was deposited as a shell respected with Pt core, and analogously, MgO was deposited as an amorphous layer onto Pt/TiO₂. As a result, high CH₄ selectivities of 85% and 83% were obtained on Cu₂O/Pt/TiO₂ and MgO-Pt/TiO₂ catalysts, respectively. In another study, a binary cocatalyst system of Ag/Pd was reported to enhance the photocatalytic activity for CO₂ to CH₄ on Ag/Pd supported on N-doped TiO₂ with a production rate of 79 μmol g⁻¹ h⁻¹ [88]. Recently, a multi-heterojunction was created on TiO₂–MnOₓ–Pt films (Figure 8). Two heterojunctions were created: A p–n junction between the MnOₓ and TiO₂ [001] facet and a metal–semiconductor junction between Pt and TiO₂ [101] facet. Thus, efficient separation of charged pairs was obtained to produce three times higher CH₄ and CH₃OH compared with the pristine TiO₂ nanosheets [89].

Another study combined some of the effective strategies mentioned above. Ye et al. fabricated a photocatalyst using hydrous hydrazine Au–Cu bimetal as the cocatalyst supported on SrTiO₃/TiO₂ coaxial nanoarchitecture arrays to create a heterojunction with fast electron-transfer [97]. As a result, excellent performance was reported on the catalyst with CO as the main product with a production rate of 3770 μmol g⁻¹ h⁻¹ along with a CH₄ production rate of 421.1 μmol g⁻¹ h⁻¹. Remarkably, the production of C₂+ products (C₂H₆: 190.1, C₂H₄: 73.3, C₃H₆: 40.8 μmol g⁻¹ h⁻¹, respectively) is very noticeable due to the formation of C₂+ products with higher values in industry from photoreduction of the problematic CO₂ gas. This research can be a representative study that manipulated various approaches to achieve a high production rate for photoreduction of CO₂, shedding light on the hybrid nanostructured design for further enhancement of the rate in the future.
with the detection of some intermediates including CO$_2^-$, Cu-CO, and carbon deposits on the surface (Figure 9).

Many applications from SPR have recently emerged as an efficient approach to advance the conversion of water and CO$_2$ [90–92]. The enhanced activity of plasmonic effect-related photocatalysts is ascribed to the direct charge transfer mechanism or the enhancement of the local electric field induced on the noble metallic atoms. Ag was loaded on TiO$_2$ nanotube arrays to improve CH$_4$ formation from photoreduction of CO$_2$ under visible light. The improved light absorption from the nanotube arrays of TiO$_2$ combined with the deposition of Ag NPs inside TiO$_2$ nanotubes was believed to cause the plasmonic effect with hot electron generation [93].

In addition, Au is also known to exhibit the SPR effect on TiO$_2$. The synergistic combination of the SPR effect from Au NPs and the role of Pt as electron-sink on nanohybrid Au/Pt co-decorated on TiO$_2$ nanofibers was reported for visible-light harvesting and was found to hinder charge recombination of photexcited TiO$_2$ [94]. Tahir synthesized montmorillonite (MMT) dispersed Au/TiO$_2$ nanocatalysts through a simple sol-gel method [95]. The photocatalytic performance of MMT-dispersed Au/TiO$_2$ under simulated solar light was enhanced because of the SPR effect of Au, catalyzing photoreduction of CO$_2$ to CO with a high production rate of 1223 $\mu$mol g$^{-1}$ h$^{-1}$. Remarkably, Garcia et al. fabricated Au–Cu alloy nanoparticles supported on TiO$_2$ to achieve excellent performance [96]. The selectivity of electrons toward CH$_4$ evolution could reach 97% with a high production rate of approximately 2200 $\mu$mol g$^{-1}$ h$^{-1}$ under visible-light irradiation. The enhanced visible-light-harvesting ability can be ascribed to the plasmonic effect from Au. Furthermore, the presence of Cu bonding to the CO$^*$ intermediate on the photocatalyst could lead to the high selectivity of CH$_4$ through a “carbene pathway” with the detection of some intermediates including CO$_2^-$, Cu-CO, and carbon deposits on the surface (Figure 9).

3.3.2. Plasmonic Effect

One of the most useful effects induced by the incorporation of noble metals on the TiO$_2$ surface to enhance the visible-light-harvesting efficiency and charge separation is the surface plasmon resonance (SPR). Many applications from SPR have recently emerged as an efficient approach to advance the conversion of water and CO$_2$ [90–92]. The enhanced activity of plasmonic effect-related photocatalysts is ascribed to the direct charge transfer mechanism or the enhancement of the local electric field induced on the noble metallic atoms. Ag was loaded on TiO$_2$ nanotube arrays to improve CH$_4$ formation from photoreduction of CO$_2$ under visible light. The improved light absorption from the nanotube arrays of TiO$_2$ combined with the deposition of Ag NPs inside TiO$_2$ nanotubes was believed to cause the plasmonic effect with hot electron generation [93].

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Photocatalytic activity because of the fast charge transfer, long-lasting lifetime of charge carriers, and impeding electron-hole recombination [98–110]. Importantly, the carbon content was found to be correlated to the charge transfer efficiency. In their subsequent study, Zou et al. developed an in situ reduction-hydrolysis method to synthesize TiO$_2$-graphene nanosheets [100]. Using this technique, GO was reduced to graphene simultaneously from hydrolysis of Ti$^{4+}$ dihydroxy is to create a 2D sandwich-like structure. Therein, the TiO$_2$ deposited on graphene acted as a stabilizing agent for graphene nanosheets, whereas the Ti$^{3+}$ observed on TiO$_2$ NPs could trap the photoexcited electrons coupled with the suppression of the electron-hole recombination.

Next, Zou et al. prepared a hollow spherical structure from titania Ti$_{0.91}$O$_2$ and graphene nanosheets [100]. The hollow spherical structure and the unique composition enhanced the photocatalytic activity because of the fast charge transfer, long-lasting lifetime of charge carriers, and enhancement of light absorption. In agreement with this study, carbon@TiO$_2$ hollow spheres were recently reported to increase the photocatalytic activity to produce CH$_4$ and CH$_3$OH [101]. Importantly, the carbon content was found to be correlated to the charge transfer efficiency. In their subsequent study, Zou et al. developed an in situ reduction-hydrolysis method to synthesize TiO$_2$-graphene nanosheets [102]. Using this technique, GO was reduced to graphene simultaneously with the formation of TiO$_2$ from hydrolysis of Ti$^{4+}$ dihydroxy is to create a 2D sandwich-like structure. Therein, the TiO$_2$ deposited on graphene acted as a stabilizing agent for graphene nanosheets, whereas the Ti$^{3+}$ observed on TiO$_2$ NPs could trap the photoexcited electrons coupled with the suppression of the electron-hole recombination.

3.4. Hybrid TiO$_2$ Nanocomposites

The employment of other materials into TiO$_2$ photocatalysts is fruitful for CO$_2$ reduction because of supplied high active sites surface area, facilitation of charge transfer to enhance CO$_2$ adsorption, and impeding electron-hole recombination [98–108]. Liang et al. reported solvent-exfoliated graphene on GO-TiO$_2$ systems to functionalize titania for the photochemical reduction of CO$_2$ [99]. An increment in the visible-light harvesting was observed on the less defective solvent-exfoliated graphene caused by the fast-electrical mobility, accelerating the photoinduced electron transport into reactive sites.

### Figure 9
Proposed schematic illustration of the mechanism of photocatalytic CO$_2$ reduction under UV and visible light for Au–Cu alloy NPs decorated on TiO$_2$ as photocatalysts, demonstrating the crucial role of the irradiation wavelength range on product distribution. Reproduced with permission from [96]. Copyright 2014, American Chemical Society.
pair recombination. Interestingly, the photocatalysts could catalyze the photoreduction of CO$_2$ toward C$_2$H$_6$ with a production rate of 16.8 $\mu$mol g$^{-1}$ h$^{-1}$, which is different from other reported catalysts, proving that the architectural design of hybrid nanocomposites can vary product selectivity.

Among the carbon-based candidates, graphitic carbon nitrides (g-C$_3$N$_4$) with an increased concentration of nitrogen on the surface and a narrower band gap (2.7 eV) than TiO$_2$ have attracted increasing attention because of the ability for CO$_2$ activation. Cu-TiO$_2$ was dispersed on g-C$_3$N$_4$ to enhance the photocatalytic performance of CO$_2$ conversion to CH$_4$ [103]. In another study, the charge transfer between semiconducting C$_3$N$_4$ nanosheets and a Ru(II)–Re(I) binuclear complex (RuRe) was improved using rutile TiO$_2$ nanocrystals as a modifier [104]. The RuRe/TiO$_2$/NS-C$_3$N$_4$ hybrid could promote both CO formation rate and turnover number under visible-light irradiation as a result of the advanced lifetime of photoinduced electrons. Zhao et al. wrapped Pt/TiO$_2$-nanocrystals with reduced GO (rGO) to synthesize a core-shell structure. The surface residual hydroxyl on the rGO shell and the extended $\pi$ bonds proved to increase the CO$_2$ adsorption and activation, while the whole hybrid core-shell structure enhanced the electron transfer and the separation efficiency to highly selective production of CH$_4$ up to 99.1% with a production rate of 41.3 $\mu$mol g$^{-1}$ h$^{-1}$ [105].

Recently, Petit et al. employed carbon nitride nanosheets (CNNS) from g-C$_3$N$_4$ and grew TiO$_2$ and control its facets on CNNS, favoring the formation of [001] facets because of their enhanced photocatalytic activity [106]. The hybrid TiO$_2$/CNNS heterostructures exhibited superior CO$_2$ adsorption and charge transfer acceleration, resulting in the availability of photoexcited electrons under UV-Vis illumination, which is 10-fold higher compared with that exhibited by pristine materials. Transient absorption spectroscopy analyses showed that the hole transfer from TiO$_2$ to CN was observed. The interfacial charge transfer via the heterojunction could inhibit the recombination of paired charges (Figure 10). This revealed that the fine control of TiO$_2$ facets could lead to a high activity for photoreduction of CO$_2$ associated with a hybrid nanocomposite structure with carbon nitride materials, thus enabling charge transfer to enhance CO$_2$ adsorption, and impeding electron-hole recombination can be a promising method to increase the production rate.

![Figure 10.](image-url)

**Figure 10.** (a) Scheme of the synthesis procedure used to produce TiO$_2$/CNNS composites. (b) Transient absorption spectroscopy spectra used to study the photoexcitation processes in powdered samples at different delay times of TiO$_2$ nanosheets (TiO$_2$-NS) following photoexcitation. Initial spectra at 1 $\mu$s for (c) TiO$_2$-NS, (d) Ti-NS/CN (synthesized in the presence of HF), and (e) Ti-ISO/CN (synthesized in the absence of HF). The hole contribution is shaded in blue, and the electron contribution is shaded in red. The sum of the two is indicated as the total (green line) compared with the experimental values shown in the black line and squares. (f) Photocatalytic CO$_2$ reduction reaction pathway for the TiO$_2$/CNNS nanocomposites improved by hole transfer from TiO$_2$-NS to CNNS. Reproduced with permission from [106]. Copyright 2019, Elsevier.
Lately, Barbieri et al. reported a continuous operating system employing C₃N₄-TiO₂ Nafion photocatalytic membrane reactors to examine the effects of crucial parameters including reaction pressure, H₂O/CO₂ feeding ratio, or contact time on the performance and selectivity of various detected products from photoreduction of CO₂ (MeOH and HCHO) [107].

Similarly, in another work, P-O linked Z-scheme g-C₃N₄/TiO₂ nanotube composites were fabricated to enhance the visible-light harvesting capability and the charge separation caused by g-C₃N₄ and P-O links [108]. CO₂ photoreduction yielded 46.9 mg L⁻¹ h⁻¹, 38.2 mg L⁻¹ h⁻¹, and 28.8 mg L⁻¹ h⁻¹ of acetic, methanol, and formic acid, respectively, which was ~3.3, 3.5, and ~3.8 times the production from TiO₂ nanotubes.

3.4.2. Other Composites

Xu et al. employed an in situ hydrothermal method to deposit CuInS₂ nanoplates onto TiO₂ nanofibers to achieve the Z-scheme TiO₂/CuInS₂ heterostructure; excellent photoreduction activity of CO₂ to CH₄ and CH₃OH under light irradiation was observed [109]. A mechanism was proposed for the high activity of TiO₂/CuInS₂ based on the direct Z-scheme heterojunction, in which photoexcited electrons from the TiO₂ CB could be transferred and recombined with the hole of CuInS₂ VB, whereas electrons generated on CuInS₂ were catalyzed for the photoreduction of CO₂ (Figure 11).

![Figure 11](image-url)

**Figure 11.** SEM images of (a,b) pristine TiO₂, (c,d) sensitized CuInS₂/TiO₂. TEM image of (e) pristine TiO₂ and (f) sensitized CuInS₂/TiO₂. (g) Energy dispersive X-ray (EDX) element mapping of Ti, O, Cu, In, and S. (h) Scheme of the illustrated charge transfer and separation in the optimum sensitized CuInS₂/TiO₂ photocatalyst under simulated sunlight irradiation. Reproduced with permission from [109]. Copyright 2018, Elsevier.

The introduction of two-dimensional inorganic compounds, MXene, as a supporter for TiO₂ was investigated. Yu et al. grew TiO₂ NPs on Ti₃C₂ in situ by calcination. An ultrathin fluffy rice crust-like structure was observed on the composite, which is beneficial for high surface for active sites. In addition, the highly conductive Ti₃C₂ assisted photoexcited electron transfer and prevented paired charge recombination. As a result, the TiO₂/Ti₃C₂ composite achieved a 3.7 times higher CH₄-production rate than commercial TiO₂ (P25) [110].
4. Conclusions and Perspective

Photoreduction of CO$_2$ is an attractive approach to utilize CO$_2$ gas for producing value-added carbon chemicals to achieve multiple purposes. This method has several advantages such as contributing to the energy demands using CO$_2$ as a significant carbon resource, diminishing environmental issues from CO$_2$, and leveraging clean, renewable energy from sunlight. To mimic natural photosynthesis, in which solar energy is used to convert CO$_2$ and H$_2$O to carbohydrates and oxygen, artificial photosynthesis was performed to develop photocatalysts, which play an identical and sophisticated role like terrestrial plants to efficiently harvest sunlight and separate the photogenerated charges for reactions for the conversion of CO$_2$ and H$_2$O into energetic chemicals. Overall, highly efficient photoreduction of CO$_2$ to fuels can be achieved by a combination of some critical strategies, including: High adsorption and activation of CO$_2$, large surface areas for active sites, efficient sunlight harvesting, generation of photoexcited electron-hole pairs, accelerated charge transfer to reactive site, and effective inhibition of charge recombination. The present review reveals the significant recent progress on TiO$_2$-based photocatalysts and decisive factors for photocatalytic performance via some critical strategies in Table 2.

| Photocatalysts | Reaction Conditions | Production Rate (µmol g$^{-1}$ h$^{-1}$) | Reference (Year) |
|----------------|---------------------|----------------------------------------|------------------|
| Anatase TiO$_2$ by coexposed [001] and [101] facets | 300 W Xe lamp TiO$_2$-NaHCO$_3$-HCl (solid-liquid) | CH$_4$: 1.35 | [52] (2014) |
| Cubic anatase TiO$_2$ nanocrystals (100 ± 13 nm) | 300 W Xe lamp TiO$_2$-H$_2$O-CO$_2$ (solid-liquid) | CH$_4$: 4.56 CH$_3$OH: 1.48 | [53] (2015) |
| TiO$_2$ nanosheets with exposed [001] facet | 2 × 18 W Hg lamps TiO$_2$-H$_2$O-CO$_2$-NaOH (solid-liquid) | CH$_4$: 0.2 CO: 0.12 CH$_3$OH: 0.19 HCHO: 0.066 | [54] (2014) |
| Flame-annealed TiO$_2$ nanotubes formed in aqueous electrolyte | AM 1.5G, 100 mW cm$^{-2}$ Catalysts-H$_2$O-CO$_2$ (solid-gas) | CH$_4$: 156.5 | [56] (2019) |
| Nanotubes/nanowires assembled from TiO$_2$ nanoflakes with [111] facet | 300-W Xe lamp TiO$_2$-H$_2$O-CO$_2$-(CH$_3$)$_2$CHOH (solid-gas) | CH$_4$: 1708.1 CO: 463.2 | [57] (2019) |
| Highly dispersed titanium oxide on mesoporous SBA-15 (Ti-SBA-15) | 100-W Hg lamp (>250 nm) TiO$_2$-H$_2$O-CO$_2$ (solid-liquid) | CH$_4$: 106 CH$_3$OH: 27.7 | [61] (2005) |
| Oxygen-deficient blue TiO$_2$ nanocrystals with coexposed [101] and [001] facets | 100-W Hg lamp 450-W Xe lamp TiO$_2$-H$_2$O-CO$_2$ (solid-gas) | CO: 55 (UV-VIS) CO: 27 (Visible light) | [66] (2016) |
| Cu and V co-doped TiO$_2$ (P25) deposited on polyurethane Cu@V/TiO$_2$-PU | Visible light (2 × 20 W white bulbs) Catalysts-H$_2$O-CO$_2$ (solid-gas) | CH$_4$: 933 CO: 588 | [72] (2017) |
| 3% NaOH-surface modification TiO$_2$ (ST01) | 300-W Xe lamp Catalysts-H$_2$O-CO$_2$ (solid-gas) | CH$_4$: 8.7 | [73] (2014) |
| 5 ultrathin MgO layers deposited on porous TiO$_2$ mixed anatase-rutile phases by atomic layer deposition | 450-W Xe lamp Catalysts-H$_2$O-CO$_2$ (solid-gas) | CO: 54 | [76] (2019) |
Table 2. Cont.

| Photocatalysts                                      | Reaction Conditions                        | Production Rate (µmol g⁻¹ h⁻¹) | Reference (Year) |
|----------------------------------------------------|-------------------------------------------|--------------------------------|-----------------|
| TiO₂-0.5% Ag                                       | 100-W Xe lamp (320–780 nm) Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 2.1                      | [75] (2014)     |
| TiO₂-0.5% Au                                       | 100-W Xe lamp (320–780 nm) Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 3.1                      | [75] (2014)     |
| TiO₂-0.5% Rh                                       | 100-W Xe lamp (320–780 nm) Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 3.5                      | [75] (2014)     |
| TiO₂-0.5% Pd                                       | 100-W Xe lamp (320–780 nm) Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 4.3                      | [75] (2014)     |
| TiO₂-0.5% Pt                                       | 100-W Xe lamp (320–780 nm) Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 4.3                      | [75] (2014)     |
| 1-D nanostructured TiO₂ single crystals loaded with Pt nanoparticles | 400-W Xe lamp Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 1361 CO: 200             | [35] (2012)     |
| Ag-Pd on N-doped TiO₂ NSs                          | 300-W Xe lamp Simulated sunlight Catalysts-H₂O-CO₂ (solid-liquid) | CH₄: 79                       | [88] (2018)     |
| Montmorillonite (MMT) dispersed Au/TiO₂ nanocatalyst | Simulated sunlight Catalysts-H₂O-CO₂ (solid-gas) | CO: 1223                      | [95] (2017)     |
| TiO₂ powder (Degussa P25) loaded with Au–Cu alloy nanoparticles | 1000-W Xe lamp Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 2200                      | [96] (2014)     |
| Au–Cu bimetal as cocatalyst supported on SrTiO₃/TiO₂ | 300-W Xe lamp Catalysts-H₂O-CO₂ (solid-gas) | CO: 3770 CH₄: 421.2 C₂H₆: 190.1 C₂H₄: 73.3 C₃H₆: 40.8 | [97] (2015)     |
| TiO₂-graphene 2D sandwich-like hybrid nanosheets    | 500-W Xe lamp Catalysts-H₂O-CO₂ (solid-gas) | C₂H₆: 16.8 CH₄: 8             | [102] (2013)    |
| 2.5% CuInS₂/TiO₂                                   | 350-W Xe lamp Catalysts-H₂O-CO₂ (solid-gas) | CH₄: 2.5 CH₃OH: 0.86          | [109] (2018)    |
| TiO₂/carbon nitride nanosheet nanocomposites       | 300-W Xe lamp (>325 nm) Catalysts-H₂O-CO₂ (solid-gas) | CO: 1.96                      | [106] (2019)    |

The architectural structure design of photocatalysts, including crystal phases, oriented facets, and dispersion of TiO₂ active sites, can play a crucial role in driving the CO₂ reduction pathways and improving photocatalytic activity. Recently, tremendous achievements have been reported with respect to the influential structure of TiO₂ rutile and anatase phases, morphology, size, various facets including [101], [001], [110], and [111], and alternative methods for TiO₂ dispersion on porous materials to improve their intrinsic photoactivities. Moreover, the introduction of oxygen defects/vacancies and functional basic sites into the TiO₂ surface can modify intermediate affinity and significantly improve CO₂ adsorption and activation ability for CO₂ reduction. Importantly, the utilization of cocatalysts such as noble metals, transition metals, and their oxides via plasmonic effects or/and heterojunctions.
improves visible-light harvesting, increases charge separation efficiency, and impedes electron-hole recombination. Furthermore, TiO$_2$-based hybrid nanocomposites with advanced performances have emerged recently by manipulating several efficient approaches mentioned above combined with the hybridization with other materials (e.g., graphene, GO, rGO, g-C$_3$N$_4$ and its derivatives, sensitized-materials, and 2D MXene) to overcome the limitations of Ti and TiO$_2$-based materials, exhibiting a CO$_2$ photoreduction production rate of some thousands of micromoles per gram per hour.

Nonetheless, further improvement of CO$_2$ adsorption, activation, and visible-light harvesting needs to be examined to enhance the sunlight harvesting yield and rate of production, which is, however, still far from practical applications. Insights on the reaction mechanism should also be investigated via in situ measurements with several powerful techniques for understanding and controlling reaction pathways, resulting in high selectivity of major products. In addition, most of studies reported the popular distribution of C1 products (CH$_4$, HCOOH, CH$_3$OH), especially CH$_4$, from photoreduction of CO$_2$ while there is a lack of the formation of C2+ products with higher price and demand in industry although a few studies exhibited the formation of C$_2$H$_4$, C$_2$H$_6$, and C$_3$H$_8$ as mentioned above (see Table 2). However, the production of C2+ products is much more complex, which requires a deeper understanding of mechanism and control. Furthermore, mass transfer and charge transfer should be comprehensively considered by examining the influence of operating parameters, structure of photocatalysts, and reactor design and operation to enable advanced yield and efficiency of sustainable CO$_2$ photoreduction.

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