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Abstract: The photocatalytic reduction of carbon dioxide to renewable fuel or other valuable chemicals using solar energy is attracting the interest of researchers because of its great potential to offer a clean fuel alternative and solve global warming problems. Unfortunately, the efficiency of CO\textsubscript{2} photocatalytic reduction remains not very high due to the fast recombination of photogenerated electron–hole and small light utilization. Consequently, tremendous efforts have been made to solve these problems, and one possible solution is the use of heterojunction photocatalysts. This review begins with the fundamental aspects of CO\textsubscript{2} photocatalytic reduction and the fundamental principles of various heterojunction photocatalysts. In the following part, we discuss using TiO\textsubscript{2} heterojunction photocatalysts with other semiconductors, such as C\textsubscript{3}N\textsubscript{4}, CeO\textsubscript{2}, CuO, CdS, MoS\textsubscript{2}, GaP, CaTiO\textsubscript{3} and FeTiO\textsubscript{3}. Finally, a concise summary and presentation of perspectives in the field of heterojunction photocatalysts are provided. The review covers references in the years 2011–2021.

Keywords: CO\textsubscript{2} reduction; heterojunction nanocomposite; TiO\textsubscript{2}; photocatalysis; renewable fuel; valuable chemicals

1. Introduction

Since the 18th century, together with the fast development of human society and the extensive use of fossil energy, environmental pollution has become increasingly serious with great environmental, social and economic impacts. Emissions of CO\textsubscript{2} and other greenhouse gases are steadily increasing. The anthropogenic source of greenhouse gas emissions is fossil fuels combustion, mainly coal, natural gas, and oil, along with soil erosion and deforestation. These gases warm the planet by trapping heat in the atmosphere and are the principal factor in global warming. The average increase in temperature since the preindustrial age has already reached almost one degree Celsius, and this rise looks set to continue [1].

The chance of CO\textsubscript{2} transformation into clean fuel could provide a progressive solution for both the future deficiency of fossil fuels and problem with global warming. In recent years, a large number of methods, such as chemical, electrochemical, biochemical, photochemical, and thermochemical techniques, have been developed for converting CO\textsubscript{2} to light hydrocarbons and alcohols [2,3]. Among the varied methods, CO\textsubscript{2} photocatalytic reduction has been receiving great attention and proved to be a promising alternative technology, once it is possible to produce greener gases and/or gases with industrial and fuel applications, using sunlight to activate the semiconductor materials, which result in the photoreduction of gaseous pollutants. This method is one of the promising processes, which not only remove carbon dioxide, but can also transform it into energy valuable products, such as methane, formaldehyde, methanol, CO and other useful compounds [4–7].

Photocatalysis can be defined as a change in the rate of a photochemical reaction by the activation of a photocatalyst (semiconductor) with sunlight or artificial light (ultraviolet or visible radiation). This process is very efficient and attractive from the economical and
eco-friendly point of view. This method is based on the use of a photocatalyst, usually a semiconductor, illuminated with energy equal to or higher than its energy of the bandgap.

It is well known that CO\textsubscript{2} is an extremely stable molecule with high thermodynamic stability, being that its reduction is extremely complicated. The photocatalytic reduction of CO\textsubscript{2} has complex reaction mechanisms and pathways involving a proton-assisted multi-electron reduction process with high energy barriers, complicated activation and CO\textsubscript{2} adsorption, and selectivity of different products as shown in Table 1.

### Table 1. Main products of CO\textsubscript{2} reduction and the corresponding potential (pH = 7).

| Reaction | $E^\circ$ (V vs. NHE) | Product | Reference |
|----------|-----------------------|---------|-----------|
| $\text{H}_2\text{O} + 2e^- \rightarrow 2\text{OH}^- + \text{H}_2$ | −0.41 | Hydrogen | [8] |
| $\text{CO}_2 + \text{e}^- \rightarrow \text{CO}^-_2$ | −1.90 | $\text{•CO}_2$ anion radical | [9] |
| $2\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{H}_2\text{C}_2\text{O}_4$ | −0.87 | Oxalate | [8] |
| $\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{HCOOH}$ | −0.61 | Formic acid | [10] |
| $\text{CO}_2 + 2\text{H}^+ + 2e^- \rightarrow \text{CO} + \text{H}_2\text{O}$ | −0.53 | Carbon monoxide | [9,10] |
| $\text{CO}_2 + 4\text{H}^+ + 4e^- \rightarrow \text{HCHO} + \text{H}_2\text{O}$ | −0.48 | Formaldehyde | [8–10] |
| $\text{CO}_2 + 6\text{H}^+ + 6e^- \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O}$ | −0.38 | Methanol | [9,10] |
| $2\text{CO}_2 + 12\text{H}^+ + 12e^- \rightarrow 3\text{H}_2\text{O} + \text{3H}_2\text{O}$ | −0.33 | Ethanol | [8] |
| $2\text{CO}_2 + 14\text{H}^+ + 14e^- \rightarrow \text{CH}_4 + 4\text{H}_2\text{O}$ | −0.27 | Ethane | [8] |
| $\text{CO}_2 + 8\text{H}^+ + 8e^- \rightarrow \text{CH}_4 + 2\text{H}_2\text{O}$ | −0.24 | Methane | [8–10] |

The photocatalytic system for the reduction of CO\textsubscript{2} makes use of a photocatalyst suspension in a solvent with dissolved carbon dioxide, and irradiation with solar energy can drive the photoreduction of CO\textsubscript{2}. Hole scavengers, such as H\textsubscript{2}O\textsubscript{2}, Na\textsubscript{2}SO\textsubscript{3}/Na\textsubscript{2}S\textsubscript{2}, CH\textsubscript{3}OH, and triethanolamine, are ordinarily added to the reaction mixture to decrease the electron–hole recombination and avoid reoxidation by generated holes or the oxygen which is produced from water [9].

Inoue et al. reported, in 1979, CO\textsubscript{2} photocatalytic reduction using several semiconductors (dispersed in water) as photocatalysts. They studied TiO\textsubscript{2}, WO\textsubscript{3}, CdS, ZnO, GaP, and SiC for the photocatalytic reduction of CO\textsubscript{2}, and concluded that TiO\textsubscript{2} and SiC materials had higher photocatalytic activity for this reaction [11]. Recently, several photocatalysts, such as TiO\textsubscript{2}, g C\textsubscript{3}N\textsubscript{4}, ZnIn\textsubscript{2}S\textsubscript{4}, Bi2WO\textsubscript{6}, graphene (GR), CdS, SrNb\textsubscript{2}O\textsubscript{6}, and ZnO, were investigated for CO\textsubscript{2} photocatalytic reduction. However, the TiO\textsubscript{2} is the most prevalently used due to its chemical stability, resistance toward corrosion, and mainly low cost [12].

TiO\textsubscript{2} has naturally three polymorphic phases: brookite, anatase, and rutile [13]. TiO\textsubscript{2} has a large band gap and, therefore, the solar light utilization rate of TiO\textsubscript{2} is only 4%. Therefore, the photocatalytic performance of TiO\textsubscript{2} using solar energy is limited [14]. TiO\textsubscript{2} has a relatively high recombination rate of photoinduced electron/hole ($e^-/h^+$) pairs [10]; hence, only a fraction of the generated $e^-/h^+$ pairs are available for photoreaction [15–17]. In recent years, there has been an effort to increase the photocatalytic activity of TiO\textsubscript{2}. Several strategies have been suggested to efficiently separate pairs of photogenerated electrons and holes in semiconductor photocatalysts, thereby increasing the efficiency of photocatalysis. Some of the most important ones are, for example, doping metals or non-metals, or creating photocatalysts with heterojunction. The formation of heterojunction photocatalysts, where the generated electron–hole pairs are efficiently separated, has emerged as one of the most promising approaches (Figure 1).

A heterojunction is the interface between two diverse materials which has a different band structure, and it can lead to band alignments. Many types of heterojunctions have been studied that are efficient for increasing the photocactivity of materials. These include conventional heterojunctions (type-I, type-II and type-III, surface heterojunctions, p–n heterojunctions, direct Z-scheme heterojunctions, and graphene-semiconductor (graphene–SC) heterojunctions [18]. In the conventional heterojunction photocatalysts, there are three types: the type-I have a straddling gap (Figure 2a), type-II have a staggered gap (Figure 2b), and the type-III a broken gap (Figure 2c).
Figure 1. Schematic illustration of the electron–hole separation on an example of heterojunction photocatalyst type-II. Adapted according to refs. [18,19].

(a) Straddling gap (type-I)  
(b) Staggered gap (type-II)  
(c) Broken gap (type-III)

Figure 2. Schematic illustration of the three different types of separation of electron–hole pairs in the case of conventional light-responsive heterojunction photocatalysts: (a) type-I, (b) type-II, and (c) type-III heterojunctions. Adapted according to Refs. [18,19].
Figure 2a shows the type-I heterojunction photocatalyst. The valence band (VB) and the conduction band (CB) of the semiconductor A are, respectively, lower and higher than the matching bands of semiconductor B. For that reason, after irradiation, e\(^-\) and h\(^+\) cumulate at the CB and the VB levels of the semiconductor B, which has lower Eg. Since both e\(^-\) and h\(^+\) cumulate on one and the same semiconductor, they cannot be effectively separated; therefore, it is not suitable for application in photocatalysis. Figure 2b represents the type-II heterojunction photocatalyst. The VB and the CB levels of semiconductor A are higher than the matching VB and CB levels of semiconductor B. In this case, the migration of photogenerated charges can occur in opposite directions, namely, the e\(^-\) are accumulated in one semiconductor, while the h\(^+\) are accumulated in the other semiconductor, resulting in a spatial separation of e\(^-\) / h\(^+\) pairs. This separation prevents the rapid recombination of photogenerated charges. A semiconductor with appropriate band positions acts as a scavenger of e\(^-\) and h\(^+\)\(^\)\, allowing these charges to react separately. The type-III, as can be seen in Figure 2c, has an architecture similar to the type-II heterojunction photocatalyst; however, there is no overlapping of band gaps, thereby being inadequate for photocatalytic applications [18,19].

The p–n heterojunction (Figure 3) combines the p-type semiconductor and n-type semiconductor. The Fermi level is closer to the valence band in a p-type semiconductor. On the other hand, in the case of an n-type semiconductor, it will shift toward the conduction band [18]. This configuration can increase migration of the electron–hole through the heterojunction for increasing the photocatalytic efficiency by giving an additional electric field. In this type of heterostructure, before light irradiation, the e\(^-\) on the n-type semiconductor diffuse across the p–n interface to the p-type semiconductor, abandoning positive holes (h\(^+\)). In the meantime, the positive holes of the p-type semiconductor diffuse into the n-type semiconductor, abandoning negative electrons. This diffusion of electrons and holes continues until the Fermi levels of the semiconductors are equal. As a result, an internal electric field is formed on the p–n interface. The electrons and holes, which are photogenerated in p-type and n-type semiconductors, travel due to the impact of the internal electric field from the conduction band of the n-type to the valence band of the p-type, respectively, following the spatial separation of electrons and holes, and prolong their lifetime. Consequently, the efficiency of e\(^-\)/h\(^+\) separation in the case of the p–n heterojunction is quicker than that of type-II heterojunction photocatalysts because of the synergic effect of the band alignment and the internal electric field [18]. For instance, it is very often that the combination of TiO\(_2\) (n-type) with a p-type semiconductor for the formation of a p–n heterojunction occurs [10].

However, for these types of heterojunctions mentioned above (conventional type-II and p–n heterojunction types), the redox capability of the photocatalyst is decreased, due to the oxidation and reduction processes take place on the semiconductor with lower oxidation and reduction potentials, respectively [10,18].

Another type of heterojunction is the Z-scheme photocatalytic system. The Z-scheme system for a liquid phase was reported in 1979 by A. J. Bard [20]. Since this discovery, the Z-scheme heterojunctions have become one of the major topics of interest for scientific researchers, to overcome the problems of the abovementioned heterojunction photocatalysts, such as the redox ability of the material [18].

The conventional Z-scheme photocatalytic system is formed with two semiconductors (PS I and PS II), which are not in physical contact, and a dissolved redox mediator consisting of an electron acceptor/donor (A/D) pair (Figure 4a). During the photocatalytic reaction, photogenerated electrons migrate from the CB of the PS II to the VB of the PS I through an A/D pair via following redox reactions.
The conventional Z-scheme photocatalytic system is formed with two semiconductors (PS I and PS II) connected by a solid mediator. This mediator can lead the electrons to go from the oxidative photocatalyst to the acceptor (A) forming an electron donor (D) (Eq 1).

In this type of heterojunction, electron separation and a redox reaction takes place, which results in effective separation of electrons and holes.

Therefore, the acceptor (A) is reduced to a donor (D) when the electrons travel due to the impact of the internal electric field, which continues until the Fermi levels of the semiconductors are equal. As a result, both oxidative and reductive photocatalysts are photoexcited, producing photogenerated electrons and holes.

Figure 3. Schematic illustration of the electron–hole separation under the influence of the internal electric field of a p–n heterojunction photocatalyst under light irradiation. Adapted according to Refs. [18,19].

Figure 4. Schematic representation of (a) electron–hole separation on the conventional Z-scheme photocatalytic system; (b) the electron–hole separation on all-solid-state Z-scheme photocatalysts; and (c) electron–hole separation on a direct Z-scheme heterojunction photocatalyst. Adapted according to Refs. [18,19].
The conventional Z-scheme photocatalytic system is formed with two semiconductors (PS I and PS II). Unfortunately, this type of heterojunction photocatalyst has the one limitation; they can solely be used in the liquid phase, in which they are not in physical contact, and an electron acceptor/donor (A/D) pair (Figure 4a), named the redox mediator. In this case, both oxidative and reductive photocatalysts are photoexcited, producing electrons and holes. After that, an \( e^- \) photogenerated in the oxidative photocatalyst reacts with the A, forming an electron donor (D) (Equation (1)). Furthermore, a hole in the reductive photocatalyst reacts with the D, producing an electron acceptor (Equation (2)).

\[
\text{Acceptor} + e^- \rightarrow \text{Donor} \tag{1}
\]

\[
\text{Donor} + h^+ \rightarrow \text{Acceptor} \tag{2}
\]

Therefore, the acceptor (A) is reduced to a donor (D) when it reacts with the electrons from the conduction band of the photocatalyst I. Then, the donor (D) is oxidized and produces the acceptor (A) due to the reaction with the holes from the valence band.

In this type of heterojunction, electron–hole separation and a redox ability is achieved, due to the fact that electrons are cumulated in photocatalyst I, with higher reduction potential, while holes are cumulated in photocatalyst II, with higher oxidation potential. The conventional Z-scheme photocatalysts can only be constructed in the liquid phase, thereby limiting their wide application in photocatalysis [18,19].

Later, in 2006, Tada et al. [21] suggested a solid-state Z-scheme photocatalytic system consisting of two photocatalysts (PS I and PS II) connected by a solid-phase electron mediator. This mediator can lead the electrons to go from the oxidative photocatalyst to the reductive photocatalyst, eliminating the inactive charge carriers [19]. Furthermore, this system (Figure 4b) can be applied in practically all experimental conditions, markedly extending it using. However, noble metals (such as Pt, Ag, and Au), which are rare and expensive, are used usually as mediators of electrons in this system, being a limitation to their practical application. In addition, this type of mediator can also absorb incident light, decreasing the photocatalyst’s light utilization [18,19].

In 2013, Yu et al. [22] suggested a heterojunction photocatalyst with the direct Z-scheme. In this case, there is a combination of two different photocatalysts, without an electron mediator. Figure 4c shows that the construction of this direct Z-scheme is the same as the all-solid-state Z-scheme, except that the rare and expensive electron mediators are not required in this system [18,19]. Similarly, \( e^- \) and \( h^+ \) are spatially separated on the material with the higher reduction potential and oxidation potential of the direct Z-scheme heterojunction photocatalyst, respectively. The fabrication cost of this direct Z-scheme is low and comparable to that of conventional type-II heterojunction systems. Furthermore, the electron–hole transfer on the direct Z-scheme heterojunction is physically more favorable than that on the type-II heterojunction due to the electrostatic attraction between electrons and holes. In particular, in the case of the direct Z-scheme photocatalysts, the transfer of \( e^- \) from the CB of the PS II to the \( h^+ \) rich VB of the PS I is easier, due to the electrostatic attraction between the electrons and the holes. Moreover, without the use of liquid-phase or noble metal electron mediators, the direct Z-scheme photocatalysts have greater potential for wide practical applications [18,19].

The structure of a direct Z-scheme catalyst and p–n heterojunction is similar to that of a type-II heterojunction catalyst. For that reason, it is essential to study the charge-carrier migration mechanism for the different types of heterojunction photocatalysts through various characterization methods, so as to differentiate them. Therefore, various characterization methods could be used for this purpose, such as radical scavenging, photocatalytic reduction testing, metal loading, X-ray photoelectron spectroscopy (XPS), effective mass calculation, internal electric-field simulation and effective mass calculation. Using only a single characterization method cannot provide exact information on the charge-carrier migration mechanism for the heterojunction photocatalyst. Therefore, a comprehensive in-
vestigation through a combination of different characterization methods is always essential to describe the type of heterojunction photocatalysts [10,18].

In this review, the most promising semiconductors with heterojunction with TiO$_2$ photocatalysts for CO$_2$ photoreduction, such as C$_3$N$_4$ [23–33], CeO$_2$ [34–38], CuO [39–43], CdS [44–47], MoS$_2$ [48–51], and others [52–54], are summarized.

2. TiO$_2$ Heterojunction Photocatalysts

2.1. g-C$_3$N$_4$/TiO$_2$

Graphitic carbon nitride (g-C$_3$N$_4$) is a metal-free organic semiconductor, with special physicochemical properties, such as photocatalytic stability [55], electronic band structure, sufficient negative potential of conduction band, chemical and high thermal stability, and low cost. Due to its optical bandgap size (~2.7 eV), it can be activated by visible light, being an appropriate solar light harvesting photocatalyst [56–58]. However, this has some disadvantages that reduce its photocatalytic activity, such as high recombination of photogenerated charge carriers, low surface area, and low electrical conductivity [59]. These disadvantages can be overcome by combining them with other heterojunction semiconductors. The combination of wide-band TiO$_2$ and small-band g-C$_3$N$_4$ as a visible light sensitizer to create a heterojunction structure can mask the light response of both photocatalysts, due to the special electronic band structure [60,61]. For this reason, we can harvest more light of the sun through a coupling of g-C$_3$N$_4$ and TiO$_2$, forming a g-C$_3$N$_4$/TiO$_2$ heterojunction. In addition to the CO$_2$ photocatalytic reduction, the resulting heterojunction between TiO$_2$ and C$_3$N$_4$ is used, for example, in the photocatalytic oxidation of NO [62], and for organic pollutants degradation in waste water [63]. CO$_2$ photocatalytic reduction using g-C$_3$N$_4$/TiO$_2$ heterojunction photocatalysts are tabulated in Table 2.

Shi et al. [25] reported yTiO$_2$–x/g-C$_3$N$_4$ heterojunction photocatalysts with efficient solar-driven CO$_2$ reduction. The 0D/2D heterostructure of oxygen vacancy-abundant TiO$_2$ quantum dots referred in the g-C$_3$N$_4$ (MCN) nanosheets (TiO$_2$–x/g-C$_3$N$_4$), were synthesized by in situ pyrolysis of NH$_2$-MIL-125 (Ti) and melamine with their different mass ratios (g/g) of 5:0.4, 5:0.15, 5:0.1, and 5:0.05. The samples were named yTiO$_2$–x/MCN (y = 8, 3, 2 and 1, which is identical to the % of Ti-MOF out of melamine). All yTiO$_2$–x/MCN photocatalysts showed magnificent photocatalytic reduction performance of CO$_2$ compared with MCN. The authors concluded that the overall rapid decay of electron–hole pairs was ascribed to the interfacial charge transfer, which was attended by relaxation of recombination mediated by shallow trapped sites. Extremely fast interfacial charge transfers significantly increased charge separation. Thus, e$^-$ in shallow trapped sites could be readily trapped by carbon dioxide. Moreover, coupling with the synergetic advantage of powerful visible light absorption, high adsorption of CO$_2$ and large specific surface area, TiO$_2$–x/g-C$_3$N$_4$ demonstrated an excellent CO evolution rate. This research shows detailed insights into optimizing the heterojunction structure for robust solar CO$_2$ conversion. The 2TiO$_2$-MCN performed the highest CO formation, roughly five times that of parent g-C$_3$N$_4$. These results show that the significant photoreduction performance of CO$_2$ is also connected with the unique structures, and interface composition of the 0D/2D structure, such as defects in the photocatalyst as well as high specific surface area for enhancing CO$_2$ adsorption and supporting charge carrier separation. In these experiments, only carbon monoxide and a small amount of hydrogen were detected [25].
| Photocatalysts | Type | Prepared | Reaction Mixture | Light Source | Conditions | Yield of Products | Type of Heterojunction | Ref. |
|----------------|------|----------|------------------|--------------|------------|------------------|-----------------------|------|
| TiO$_2$-g-$\text{C}_3\text{N}_4$ | Solid state synthesis | CO$_2$ (99.999%), 5 mL of solution containing 4 mL of methyl cyanide (MeCN) solvent, 1 mL of triethanolamine (TEOA), bipyridine (bpy) (10 mmol L$^{-1}$) and 25 μL of 20 mmol L$^{-1}$ CoCl$_2$ aqueous solution | 300 W xenon lamp | CO = 23 μmol g$^{-1}$ cat.$^{-1}$ after 4 h |  | CO = 77.8 μmol g$^{-1}$ h$^{-1}$ | Type-II (see Ref. [27]) | [25] |
| (0.3/1)TiO$_2$/g-$\text{C}_3\text{N}_4$ | Simple mechanical mixing of pure g-$\text{C}_3\text{N}_4$ and commercial TiO$_2$ | CO$_2$ with a certified maximum of hydrocarbons less than 1 ppm (SIAD Technical Gases, CZ) | 8 W Hg lamp | Cylindrical stirred batch reactor, with internal volume of 355 cm$^3$ Photocatalyst concentration in 0.28 g L$^{-1}$ | CH$_4$ = 70 μmol g$^{-1}$ cat.$^{-1}$ after 8 h | Type-II | [26] |
| TiO$_2$-8%g-$\text{C}_3\text{N}_4$-20% | Stirring method | CO$_2$ and 50 mL 0.08 mol L$^{-1}$ NaHCO$_3$ solution | 300 W Xe lamp with a 420 nm optical filter | quartz glass tube with a volume of 60 mL Photocatalyst concentration in 1 g L$^{-1}$ | CH$_3$OH = 50 μmol g$^{-1}$ cat.$^{-1}$ after 4 h | Type-II (see Ref. [27]) | [27] |

**Table 2.** CO$_2$ photoreduction using g-$\text{C}_3\text{N}_4$/TiO$_2$ heterojunction photocatalysts.
Table 2. Cont.

| Photocatalysts          | CO₂ Photoreduction Condition                                                                 | Yield of Products                                                                 | Type of Heterojunction | Ref. |
|-------------------------|-----------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------|------------------------|------|
| HCNS@TiO₂               | Templating method combined with the subsequent kinetically-controlled coating process         | CH₃OH = 52.1 µmol g⁻¹cat⁻¹                                                          | Type-II                | [28] |
|                         | CO₂ (high purity) and H₂O (400 mL)                                                            | CH₄ = 21.3 µmol g⁻¹cat⁻¹ after 6 h                                                 |                        |      |
|                         | Visible-light (300 W Xenon lamp)                                                             |                                                                                   |                        |      |
|                         | cylindrical Pyrex glass photoreactor with 500 mL of volume                                   |                                                                                   |                        |      |
|                         | Photocatalyst concentration in 1 g L⁻¹                                                      |                                                                                   |                        |      |
| 70:30 g-C₃N₄-N-TiO₂     | Hydrothermal method and thermal treatment (in situ method)                                    | CO = 14.73 µmol after 12 h                                                       | Type-II                | [29] |
|                         | Deionized H₂O + CO₂ (99.999%)                                                               |                                                                                   |                        |      |
|                         | 300 W Xe arc lamp                                                                            |                                                                                   |                        |      |
|                         | Intensity 100 mW/cm²                                                                        |                                                                                   |                        |      |
|                         | 780 mL gas-closed circulation                                                               |                                                                                   |                        |      |
|                         | Teflon system                                                                               |                                                                                   |                        |      |
|                         | Photocatalyst concentration in 0.13 g L⁻¹                                                   |                                                                                   |                        |      |
| Nb-TiO₂/g-C₃N₄          | Solid state synthesis                                                                       | CO = 420 µmol g⁻¹ h⁻¹                                                             | Z-scheme               | [30] |
|                         | CO₂ (99.99%) flow rate 20 mL/min, water vapor was used as hole scavenger                     | HCOOH = 698 µmol g⁻¹ h⁻¹                                                          |                        |      |
|                         | Two 30 W white bulbs                                                                         | CH₄ = 562 µmol g⁻¹ h⁻¹                                                            |                        |      |
|                         | continuous gas system with a reactor (40 mL) located in the center of a dark cover cask     |                                                                                   |                        |      |
|                         | using as a reaction chamber (24 L)                                                          |                                                                                   |                        |      |
|                         | Photocatalyst concentration in 2.5 g L⁻¹                                                    |                                                                                   |                        |      |

Diagram: [Diagram showing photocatalyst and reaction setup]

Diagram: [Diagram showing photocatalyst and reaction setup]
### Table 2. Cont.

| Photocatalysts                  | CO₂ Photoreduction Condition                                                                 | Yield of Products | Type of Heterojunction | Ref. |
|--------------------------------|---------------------------------------------------------------------------------------------|-------------------|------------------------|------|
| 8 mass % g-C₃N₄/Ag-TiO₂         | Solvent evaporation followed by calcination CO₂ flow rate 3 mL/min; water vapor was used as hole scavenger | CH₄ = 28.0 μmol g⁻¹ | Type-II                | [31] |
|                               | 70 mL cylindrical photoreactor Photocatalyst concentration in 0.7 g L⁻¹                      | CO = 19.0 μmol g⁻¹ |                        |      |
|                               | 300 W xenon lamp                                                                          | CO = 0.138 μmol cm⁻²h⁻¹ |                        |      |
|                               | 300 W xenon lamp                                                                          | CH₄ = 40 μmol g⁻¹ h⁻¹ | Z-scheme               | [32] |
|                               | Cylindrical steel reactor (volume of 100 mL and area of 3.5 cm²) Photocatalyst concentration in 2 g L⁻¹ | CO = 15 μmol g⁻¹ h⁻¹ |                        |      |
| Phosphate–oxygen (P–O) bridged | Impregnation–solid state synthesis CO₂ + 3 mL H₂O; water vapor was used as a hole scavenger | CH₄ = 0.138 μmol cm⁻²h⁻¹ |                         |      |
| TiO₂/g-C₃N₄                   | 300 W xenon lamp                                                                          | CH₄ = 0.032 μmol cm⁻²h⁻¹ | Z-scheme               | [33] |
|                               | Cylindrical steel reactor (volume of 100 mL and area of 3.5 cm²) Photocatalyst concentration in 2 g L⁻¹ | CH₄ = 28.0 μmol g⁻¹ |                        |      |

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Reli et al. [26] studied the TiO$_2$/g-C$_3$N$_4$ materials with the ratio of TiO$_2$ to g-C$_3$N$_4$ ranging from 0.3/1 to 2/1 (TiO$_2$/g-C$_3$N$_4$ ratio of 0.3/1, 0.5/1, 1/1, and 2/1) for the photoreduction of CO$_2$ and photoreduction of N$_2$O. They reported that the production rate of methane is almost linear during the first 8 h of irradiation; on the other hand, the carbon monoxide yields increased rapidly in the first two hours and then are almost constant. The hydrogen was also detected. The hydrogen is generated from the water splitting. The most photoactive photocatalyst was (0.3/1)TiO$_2$/g-C$_3$N$_4$ in the presence of which they observed the highest yields of the products. On the other hand, the lowest product formation was achieved over pristine g-C$_3$N$_4$. The authors concluded that the highest photocactivity of the (0.3/1)TiO$_2$/g-C$_3$N$_4$ photocatalyst can be clarified by the combination of several aspects, such as adsorption edge energy, surface area (S$_{BET}$), crystallite size and efficient charge carrier separation. The key parameter is the efficient charge separation [26].

Zhang et al. [27] described the synthesis of hollow TiO$_2@g$-C$_3$N$_4$ nanocomposites for CO$_2$ photocatalytic reduction under visible irradiation. In this work was reported the utilization of four TiO$_2@g$-C$_3$N$_4$ composites with different mass ratios of g-C$_3$N$_4$ with respect to composites of 11.1%, 14.3%, 20% and 33.3%, labeled as TiO$_2@g$-C$_3$N$_4$-11.1%, TiO$_2@g$-C$_3$N$_4$-14.3%, TiO$_2@g$-C$_3$N$_4$-20%, and TiO$_2@g$-C$_3$N$_4$-33.3%, respectively. The results indicated that TiO$_2@g$-C$_3$N$_4$ photocatalysts displayed higher photocatalytic activity, compared with pure g-C$_3$N$_4$ and the TiO$_2$ does not showed photocatalytic activity under visible light irradiation. The increased photocatalytic activity of TiO$_2@g$-C$_3$N$_4$ nanocomposites was attributed to the higher photo-induced electron–hole separation efficiency and enhanced photoinduced electron migration. Furthermore, the sample with the best photocatalytic performance for the CO$_2$ reduction was the TiO$_2@g$-C$_3$N$_4$-20%. They concluded that with the decrease in g-C$_3$N$_4$ content, the yield of methanol decreased, due to the fact that TiO$_2$ has no catalytic activity in visible light, so the higher amount of TiO$_2$ weakened the absorbing ability of visible light and reduced the photocatalytic efficiency of the TiO$_2@g$-C$_3$N$_4$-11.1% and TiO$_2@g$-C$_3$N$_4$-14.3% composite materials [27].

Dehkordi et al. [28] reported a hierarchical g-C$_3$N$_4$@TiO$_2$ hollow sphere with brilliant activity for CO$_2$ photocatalytic reduction under visible irradiation. These samples have TiO$_2$ shell onto the surface of hollow carbon nitride sphere (HCNS) and are named HCNS@TiO$_2$. In this work, the photocatalytic efficiency of the HCNS@TiO$_2$ photocatalyst was compared with the commercial photocatalyst TiO$_2$ (P25), g-C$_3$N$_4$ and P25/g-C$_3$N$_4$. The obtained results showed that the P25/g-C$_3$N$_4$ and HCNS@TiO$_2$ samples had a superior efficiency for the conversion of CO$_2$ to valuable products under visible light irradiation, once P25 and pristine g-C$_3$N$_4$ showed the small yield of CH$_3$OH production due to the poor visible light activity and the fast rate of electron–hole recombination, respectively. Furthermore, the heterojunction photocatalyst formed through the combination of TiO$_2$ and g-C$_3$N$_4$ with a special hierarchical hollow structure (HCNS@TiO$_2$) showed to be promising with higher potential than each pristine photocatalysts in the CO$_2$. In this reaction, methanol was the primary product in the beginning of irradiation; consequently, the authors concluded that the solar fuel (CH$_3$OH/CH$_4$) can be obtained by the control of the reaction time of CO$_2$ photoreduction. The authors concluded that the nanocomposite photocatalytic activity could be ascribed to its special structure, providing properties, such as multiple light reflection, light harvesting, and an improved active site. They also observed that the improvement in the photocatalytic performance of the HCNS@TiO$_2$ was obtained due to the increased light absorption. The efficiency of CO$_2$ photoreduction over the HCNS@TiO$_2$ photocatalyst was approximately 5 and 10 times higher than in the presence of pristine g-C$_3$N$_4$ and P25, respectively [28]. The decisive parameter responsible for the increasing the photocatalytic performance of HCNS@TiO$_2$ photocatalyst is the synergistic heterojunction creation between the hollow g-C$_3$N$_4$ sphere with TiO$_2$, which makes a rapid electron transfer at the interface between HCNS and TiO$_2$ and increases charge carrier separation [28].

Furthermore, the interest in studying the efficiency of heterojunction materials for CO$_2$ photoreduction has been increasing, and some studies have also been reported using the combination of g-C$_3$N$_4$ with doped TiO$_2$, for instance, TiO$_2$ doped with amine species (N),...
and modified with metals, for example Ag and Au. Therefore, the most relevant reported works are mentioned here in this review.

For instance, Zhou et al. described the selective photoreduction of carbon dioxide to CO, using the graphitic carbon nitride (g-C\textsubscript{3}N\textsubscript{4})-N-TiO\textsubscript{2} heterostructure as an effective photocatalyst [29]. In this work, the authors prepared photocatalysts of graphitic carbon nitride and in situ N-modified titanium dioxide (g-C\textsubscript{3}N\textsubscript{4}-N-TiO\textsubscript{2} composites), using precursors that incorporate urea and Ti(OH)\textsubscript{4} with various mass ratios (80:20, 70:30, 60:40, 50:50, 40:60, 30:70, 20:80, and 10:90). The greater ratios of urea to Ti(OH)\textsubscript{4} (60:40 and more) result in the photocatalysts of g-C\textsubscript{3}N\textsubscript{4} and N-doped TiO\textsubscript{2}, while smaller ratios (till 50:50) only show in N-doped TiO\textsubscript{2}. The selectivity of the photocatalytic reaction is interesting in the presence of these photocatalysts. In the presence of N-doped TiO\textsubscript{2} samples, CH\textsubscript{4} and CO were generated, while in the presence of g-C\textsubscript{3}N\textsubscript{4} and N-TiO\textsubscript{2}, only CO was performed; the product selectivity may connect with the formed g-C\textsubscript{3}N\textsubscript{4}. Among the as-prepared samples, 70:30 g-C\textsubscript{3}N\textsubscript{4} and N-TiO\textsubscript{2} composites present the highest CO formation, due to the visible light absorption and lowest electrons and holes recombination. As can be seen in the CO\textsubscript{2} photoreduction reactions in Table 1, eight electrons are required for the formation of one product selectivity may connect with the formed g-C\textsubscript{3}N\textsubscript{4}.

Furthermore, when the Nb-TiO\textsubscript{2} catalytic reduction under visible irradiation was possible in the presence of Nb-TiO\textsubscript{2} due to the high recombination rates of photoexcited e\textsuperscript{−} and h\textsuperscript{+}. As can be seen in the CO\textsubscript{2} photoreduction into CO is a more dynamic, favored process. For that reason, the CO\textsubscript{2} photoreduction into CO is a more dynamic, favored process.

Based on this fact and with the obtained results, the authors designed a mechanism for the increase in photocatalytic performance, where charge carriers are created and transmitted between the interface of g-C\textsubscript{3}N\textsubscript{4} and N-TiO\textsubscript{2} during irradiation. Therefore, the holes in g-C\textsubscript{3}N\textsubscript{4} (h\textsuperscript{+} created in g-C\textsubscript{3}N\textsubscript{4} and transmitted from the valence band of TiO\textsubscript{2}) might oxidize the H\textsubscript{2}O absorbed on the surface of g-C\textsubscript{3}N\textsubscript{4}, producing O\textsubscript{2} and H\textsuperscript{+}. Furthermore, the electrons in N-TiO\textsubscript{2} (created in N-TiO\textsubscript{2} and the e\textsuperscript{−} transmitted from g-C\textsubscript{3}N\textsubscript{4}) can reduce the CO\textsubscript{2} into C1 intermediates. No methane was produced when a high ratio of urea and Ti(OH)\textsubscript{4} (60:40 or more) was used. This was due to the presence of g-C\textsubscript{3}N\textsubscript{4} and N-TiO\textsubscript{2}: the H\textsuperscript{+} may not capture the photogenerated e\textsuperscript{−}, due to the formation of aromatic heterocycles of g-C\textsubscript{3}N\textsubscript{4}, which are electron rich, where the protons can be stabilized by the conjugated aromatic heterocycles and, thus, they have difficulty in taking part in the formation of CH\textsubscript{4}. Furthermore, the e\textsuperscript{−} in the conduction band of g-C\textsubscript{3}N\textsubscript{4} can quickly be transferred to the conduction band of N-TiO\textsubscript{2} for CO\textsubscript{2} photoreduction into CO. For that reason, the g-C\textsubscript{3}N\textsubscript{4}-N-TiO\textsubscript{2} photocatalyst formed is selective for the production of CO during the CO\textsubscript{2} photoreduction. On the other hand, for low ratios of urea to Ti(OH)\textsubscript{4} (till 50:50), the H\textsuperscript{+} radicals or H\textsuperscript{+} ions formatted during CO\textsubscript{2} photocatalytic reduction can be quickly consumed by adsorbed carbon dioxide; thus, CO and CH\textsubscript{4} were simultaneously analyzed, due to the absence of conjugated aromatic system on these samples [29].

Another example of the combination of g-C\textsubscript{3}N\textsubscript{4} with doped TiO\textsubscript{2} was reported by Truc et al. [30], using TiO\textsubscript{2} doped with niobium. Truc et al. [30] studied the photoactivity of niobium doped TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} direct Z-scheme photocatalytic system for effective CO\textsubscript{2} conversion into valuable fuels. They prepared three Nb-TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} samples with 25%, 50%, and 75% of the mole percentages of Nb-TiO\textsubscript{2}.

The authors observed that g-C\textsubscript{3}N\textsubscript{4} did not reduce CO\textsubscript{2} under visible light irradiation, due to the high recombination rates of photoexcited e\textsuperscript{−} and h\textsuperscript{+}. However, CO\textsubscript{2} photocatalytic reduction under visible irradiation was possible in the presence of Nb-TiO\textsubscript{2} and Nb-TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} materials, obtaining different products (CH\textsubscript{4}, CO, and HCOOH). In the presence of a pure Nb-TiO\textsubscript{2} photocatalyst, the products were CO and CH\textsubscript{4}. Nb dopant in TiO\textsubscript{2} lattice led to the creation of the Ti\textsuperscript{3+}, which was as an intermediate band between the valence band and the conduction band of the TiO\textsubscript{2}, reducing the e\textsuperscript{−} and h\textsuperscript{+} recombination. Furthermore, when the Nb-TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} was used as photocatalyst, not only CO and CH\textsubscript{4} were produced, but also HCOOH was obtained [30].

As expected, the photocatalytic activity for CO\textsubscript{2} reduction was higher for the Nb-TiO\textsubscript{2}/g-C\textsubscript{3}N\textsubscript{4} samples, when compared to the Nb-TiO\textsubscript{2}, g-C\textsubscript{3}N\textsubscript{4} and TiO\textsubscript{2} samples. The authors attributed this to the direct Z-scheme mechanism, where photoexcited e\textsuperscript{−} in the Nb-TiO\textsubscript{2} CB combined with the photoexcited h\textsuperscript{+} in the g-C\textsubscript{3}N\textsubscript{4} VB avoided the existence of e\textsuperscript{−}.
in the g-C<sub>3</sub>N<sub>4</sub> CB and h<sup>+</sup> in the Nb-TiO<sub>2</sub> VB. Therefore, this Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> system had more available electron–hole pairs when compared with the pure Nb-TiO<sub>2</sub> photocatalyst. Furthermore, the potential energy of the generated electrons of Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> (−1.2 V) was more negative than the generated electron of Nb-TiO<sub>2</sub> (−0.2 V), so the generated electron of the Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> required lower energy during the reduction of CO<sub>2</sub> when compared with that of the Nb-TiO<sub>2</sub> [30].

The best photocatalyst for the photoreduction in CO<sub>2</sub> under visible light irradiation was the 50Nb-TiO<sub>2</sub>/50 g-C<sub>3</sub>N<sub>4</sub>. The higher efficiency of this sample was due to the higher numbers of produced and consumed e<sup>−</sup> and h<sup>+</sup> when compared with the Nb-TiO<sub>2</sub> and the other Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts. In the 50Nb-TiO<sub>2</sub>/50 g-C<sub>3</sub>N<sub>4</sub> sample, the Nb-TiO<sub>2</sub> mole resembled the mole of g-C<sub>3</sub>N<sub>4</sub>; therefore, the photogenerated electrons in the Nb-TiO<sub>2</sub> CB would achieve photogenerated holes in the g-C<sub>3</sub>N<sub>4</sub> VB. Therefore, the amounts of e<sup>−</sup> in the g-C<sub>3</sub>N<sub>4</sub> CB and h<sup>+</sup> in the Nb-TiO<sub>2</sub> VB of the 50Nb-TiO<sub>2</sub>/50 g-C<sub>3</sub>N<sub>4</sub> sample were considerably higher than in the presence of other photocatalysts. Based on this work, they concluded that the Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> photocatalysts have more charge carriers available for different valuable fuels. Additionally, the photogenerated electrons of the Nb-TiO<sub>2</sub>/g-C<sub>3</sub>N<sub>4</sub> in the conduction band of the g-C<sub>3</sub>N<sub>4</sub>, for which the potential energy is around −1.2 V, are enough strong to produce not only CO and CH<sub>4</sub>, but also HCOOH during the reduction of CO<sub>2</sub> [30].

Li et al., for example, used the heterostructured g-C<sub>3</sub>N<sub>4</sub>/Ag-TiO<sub>2</sub> photocatalyst for the CO<sub>2</sub> photocatalytic conversion [31]. These authors reported for the first time the preparation of heterostructured g-C<sub>3</sub>N<sub>4</sub>/Ag-TiO<sub>2</sub> materials via a facile solvent evaporation and by a calcination process with g-C<sub>3</sub>N<sub>4</sub> and Ag-TiO<sub>2</sub> as precursors. They prepared four different g-C<sub>3</sub>N<sub>4</sub>/Ag-TiO<sub>2</sub> samples with various masses of g-C<sub>3</sub>N<sub>4</sub> and Ag-TiO<sub>2</sub> and compared them with the commercial TiO<sub>2</sub> photocatalyst (Degussa P25), g-C<sub>3</sub>N<sub>4</sub>, and AgTi samples. As expected, the results showed that TiO<sub>2</sub> obtained the lower CO<sub>2</sub> conversion, and no significant amount of CH<sub>4</sub> was formed during the 3 h irradiation. Using g-C<sub>3</sub>N<sub>4</sub>, the CO<sub>2</sub> conversion was higher in comparison with TiO<sub>2</sub>; however, the CH<sub>4</sub> yields were still very low. The AgTi sample showed higher performance than TiO<sub>2</sub> due to the Ag nanoparticles (NPs) on the AgTi sample not only making the separation of generated charge carriers on TiO<sub>2</sub> by UV irradiation easy, but also increasing the energy of trapped e<sup>−</sup> through the Ag surface plasmon resonance effect with the visible light irradiation. Due to this fact, there were more e<sup>−</sup> with higher energy for CH<sub>4</sub> formation during CO<sub>2</sub> reduction. Using the CN/AgTi composite samples, both the conversion of CO<sub>2</sub> and solar fuel (CH<sub>4</sub> and CO) yields enhanced with the higher amount of g-C<sub>3</sub>N<sub>4</sub> to AgTi mass ratio from 0 to 8%. They also observed that the rate of electrons consumed was higher when the composite samples were used.

The results showed that the 8CN/AgTi sample (with g-C<sub>3</sub>N<sub>4</sub> to AgTi mass ratio of 8%) obtained the highest photoconversion of CO<sub>2</sub> after 3 h of irradiation. Based on this result, the authors concluded that the coupling of g-C<sub>3</sub>N<sub>4</sub> and AgTi had a synergistic effect in the photocatalytic reduction of CO<sub>2</sub>. However, when the g-C<sub>3</sub>N<sub>4</sub> to AgTi mass ratio increased to 12%, this led to an evident decrease in the photocatalytic reduction of CO<sub>2</sub>; this decreasing trend is ordinary, and it is possible to attribute it to the fact that an excessive amount of g-C<sub>3</sub>N<sub>4</sub> resulted in shielding of the active site on the TiO<sub>2</sub> surface.

The authors reported that the combination of g-C<sub>3</sub>N<sub>4</sub> and AgTi enhanced the generation of electrons and holes under sunlight. These photogenerated electrons moved through the heterojunction between carbon nitride and titanium dioxide, and further from titanium dioxide to silver nanoparticles with a lower Fermi level, avoiding the electron–hole recombination, and led to electrons cumulating on Ag nanoparticles deposited on the surface of TiO<sub>2</sub> in the g-C<sub>3</sub>N<sub>4</sub>/AgTiO<sub>2</sub>. After that, the e<sup>−</sup> cumulated on the Ag nanoparticles were further energized by the surface plasmon resonance effect. Therefore, the CN/AgTi samples showed higher photocatalytic performance.

The Ag nanoparticles on the TiO<sub>2</sub> surface in the CN/AgTi composite had a significant role once they decelerated the e<sup>−</sup>/h<sup>+</sup> pairs recombination due to extracting e<sup>−</sup> from conductive band of TiO<sub>2</sub> and also used the surface plasmon resonance effect to increase the energy level of e<sup>−</sup> cumulating on the surface. Therefore, the bounteous energetic electrons
on Ag nanoparticles generated from the activation by solar irradiation of the both TiO$_2$ and g-C$_3$N$_4$ parts were answerable for the important synergy of the combination of g-C$_3$N$_4$ and Ag/Ti in photoreduction of CO$_2$ in the presence of water vapor [31].

Liu et al. studied the P–O functional bridges effects on the electron and hole transfer and separation of TiO$_2$/g-C$_3$N$_4$ photocatalysts for the CO$_2$ reduction [32]. The authors prepared four P–O bridge TiO$_2$/g-C$_3$N$_4$ composite samples with various molar % ratios of phosphate to TiO$_2$ (1, 5, 10 and 15%) and compared them with the g-C$_3$N$_4$ and TiO$_2$/g-C$_3$N$_4$ samples. All photocatalysts exhibited excellent photocatalytic activity for CO$_2$ reduction, being that CH$_4$ was the principal product obtained as well as CO in a small amount. The sample TiO$_2$/g-C$_3$N$_4$ with the P–O bridge with 10% molar ratio showed the best performance for this reaction, with photoactivity approximately 2 and 3 times higher than for pure samples. The P–O functional bridges increased the heterojunction coupling between TiO$_2$ and g-C$_3$N$_4$, thereby significantly enhancing the charge transfer and separation, obtaining higher photocatalytic activity.

Based on this study, the authors concluded that the photoactivity of g-C$_3$N$_4$ was significantly improved due to the connection with P-O-bridged TiO$_2$ (in a proper amount). The characterization of the P–O bridge TiO$_2$/g-C$_3$N$_4$ composite samples, using surface photovoltage and photoluminescence spectroscopy, showed that the improvement on the e$^{-}$/h$^+$ separation of g-C$_3$N$_4$ after coupling with the P–O bridged TiO$_2$ resulted from the P–O bridge between TiO$_2$ and g-C$_3$N$_4$ that promotes effectively the electrons’ transference from g-C$_3$N$_4$ to TiO$_2$ [32]. Sun et al. [33] reported the preparation of a Z-scheme heterostructure with r-TiO$_2$ (rutile) modified with gold and g-C$_3$N$_4$ quantum dots to achieve a recyclable and high-efficiency photocatalyst for CO$_2$ reduction. The photocatalytic activity of (Au, C$_3$N$_4$)/TiO$_2$ composite was compared with the C$_3$N$_4$/TiO$_2$, r-TiO$_2$, and bulk C$_3$N$_4$. The obtained products were CO, CH$_4$ and O$_2$; however, using the pristine r-TiO$_2$ and bulk g-C$_3$N$_4$ samples, no significant CH$_4$ yield was observed. The higher-energy products require a higher reduction potential. Carbon dioxide reduction to methane is an 8-electrons process, which requires the photogenerated charge to have a long lifetime. The CB band of the pure r-TiO$_2$ is not negative enough to transfer CO$_2$ to CH$_4$. However, for the (Au, C$_3$N$_4$)/TiO$_2$ composite, the yield amount of carbon monoxide and methane was markedly enhanced. The authors concluded that a Z-scheme heterostructure was formed at the r-TiO$_2$ and g-C$_3$N$_4$ interface, instead of type-II heterojunction [33].

The results demonstrated that the (Au, C$_3$N$_4$)/TiO$_2$ photocatalyst has four and five times higher photoactivity in comparison with the bulk g-C$_3$N$_4$ and pristine r-TiO$_2$, respectively. This improvement on the photocatalytic performance was attributed to the excellent Z-scheme heterojunction formed in the interface of r-TiO$_2$ and g-C$_3$N$_4$ [33].

2.2. CeO$_2$/TiO$_2$

Ceria or cerium oxide (CeO$_2$) is a rare earth metal oxide that has attracted the interest of researchers due to the fact that the valences of ceria, such as Ce$^{4+}$ and Ce$^{3+}$, enhance light absorption ability and increase electron transfer. This material is an n-type semiconductor with a large bandgap energy (2.7–3.2 eV), non-toxic, readily available, and chemically stable [64]. CeO$_2$ present two oxidation states, Ce (IV) and Ce (III), which give it unique chemical, mechanical, and magnetic properties. Furthermore, the Ce (III) and Ce (IV) oxidation states can be easily converted from one to another [64,65]. The surface oxygen vacancies of CeO$_2$ from the reversible characteristics of Ce$^{3+}$ and Ce$^{4+}$ can promote its photocatalytic performance. During the reduction of Ce$^{4+}$ ions into Ce$^{3+}$, there occurs a formation of oxygen vacancies on the photocatalyst surface, which consequently act as electron trap centers that can inhibit the recombination [64]. Recently, the utilization of CeO$_2$ as a coupling was reported since the Ce$^{4+}$/Ce$^{3+}$ displacement can accelerate the charge separation and impurity levels caused by CeO$_2$ coupled TiO$_2$ to be excited in the visible region [66]. CO$_2$ photocatalytic reduction using CeO$_2$/TiO$_2$ heterojunction photocatalysts are tabulated in Table 3.
Table 3. CO₂ photoreduction using CeO₂/TiO₂ heterojunction photocatalysts.

| Photocatalysts | Preparative Method | Reaction Mixture | Photoreduction Conditions | Yield of Products | Type of Heterojunction | Ref. |
|---------------|--------------------|------------------|---------------------------|-------------------|------------------------|------|
| Max-CeTi-1.0  | Template method using a nanocasting route | CO₂ + H₂O | Xe arc lamp 300 W | CH₄ = 11.5 mmol g⁻¹ cat | Type-II | [34] |
| CeO₂-TiO₂     | Stirring method and calcination method | CO₂ and 300 mL of 0.3 mol L⁻¹ NaOH solution (for 30 min before irradiation) | Visible light—500 W Xenon lamp, and 2 mol L⁻¹ sodium nitrite solution (to remove UV light) | CH₄ = 23.5 µmol g⁻¹ after 6 h | Type-II | [35] |
| CeO₂/TiO₂-4   | Gas bubbling-assisted membrane precipitation (GBMP) method | CO₂ and H₂O | 300 W Xe lamp, and an optical filter with the absorbed light wavelength of <420 nm | CO = 41.9 µmol g⁻¹ after 6 h | Type-II | [36] |
| CeO₂/TiO₂ (0.1TeO₂) | Hydrothermal method | CO₂ and H₂O (Gaseous CO₂ of 8 kPa in situ produced by the reaction of NaHCO₃ with a H₂SO₄ solution (0.5 M).) | 500 W Xe lamp, reactor connected with mechanical vacuum pump | CO = 46.6 µmol g⁻¹ after 6 h | Type-II | [37] |
| 0.2CeO₂/TiO₂  | One-pot hydrothermal method | CO₂ and H₂O (Gaseous CO₂ of 8 kPa was produced in situ by the reaction of NaHCO₃ with a H₂SO₄ solution (0.5 M).) | 300 W Xe lamp, reactor connected with mechanical vacuum pump | CO = 30.2 µmol g⁻¹ after 6 h | Type- | [38] |

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Wang et al. [34] prepared three photocatalysts with various Ce/Ti molar ratios, 1:2, 1:1, and 2:1. All prepared CeO₂-TiO₂ composites had higher photoactivity for the CO₂ photoreduction to CH₄ and CO, when compared with Mes-CeO₂, Mes-TiO₂ and commercial TiO₂ photocatalyst (P25). This enhancement of the photocatalytic efficiency for these CeO₂-TiO₂ photocatalysts was achieved due to the ordered large specific surface area, mesoporous architecture, 2D open-pore system that facilitates the diffusion of the reactant into the bulk of photocatalyst and consequently provides fast intraparticle molecular transfer, and also due to the absorption in the visible range due to the CeO₂ species photosensitization. The heterojunction between CeO₂ and TiO₂ also contributes to the enhancement of the CeO₂-TiO₂ composites, once the photogenerated e⁻/h⁺ separation in the TiO₂ can be transferred for the CeO₂ under the internal electric field, improving the e⁻/h⁺ separation in the TiO₂, leading to the improvement of photoactivity under irradiation [34].

The authors also confirmed by XPS analysis that the presence of CeO₂ can increase significantly the chemisorbed of oxygen species on the surface of the ordered mesoporous CeO₂-TiO₂ composites. These O species can easily trap e⁻ and produce surface O• with outstanding reduction ability. Additionally, the mixture of Ce³⁺/Ce⁴⁺ oxidation states on the CeO₂-TiO₂ surface show that the partial metal in photocatalysts is not completely oxidized, and therefore, Ce³⁺ can react with holes and avoid the recombination of photogenerated e⁻/h⁺, leading to a higher quantum effectiveness of CO₂ photoreduction [34].

Comparing the efficiency of the three different composites, no significant differences were obtained in the obtained yields of CO and CH₄ after 325 min of irradiation. The authors analyzed the stability of the composites after irradiation and concluded that these composite were stable after the photocatalytic test [34].

Abdullah et al. [35] reported a CeO₂-TiO₂ composite for the photoreduction of CO₂ into CH₃OH under Vis irradiation. They demonstrated that the methanol yield in the presence of CeO₂-TiO₂ was three times higher than that of pure TiO₂. The researchers concluded that this improvement is due to the existence of active anatase phase of titanium dioxide with a small crystalline size, and the uniform structure and smaller bandgap of the CeO₂-TiO₂ photocatalyst increased the visible light absorption and produced more e⁻/h⁺ pairs. Furthermore, the existence of both Ce³⁺ and Ce⁴⁺ oxidation states on the surface of CeO₂-TiO₂ avoided the recombination of the photogenerated e⁻/h⁺. In this case, the e⁻ are captured by the Ce⁴⁺, and these trapped electrons are moved to the adsorbed oxygen in order to produce superoxide anion radicals, while Ce³⁺ reacts with the generated h⁺, reducing the e⁻/h⁺ recombination. As can be seen in the schematic representation in Table 3, the CeO₂ has a more negative CB energy, due to the possibility of photexcited e⁻ transference from CB of CeO₂ to CB of TiO₂, decreasing the recombination rate of the charge carriers [35].

Jiao et al. [36] prepared four CeO₂/TiO₂-n photocatalysts, with the weight ratio of CeO₂ to TiO₂ of n/100, obtaining the samples CeO₂/TiO₂-16, CeO₂/TiO₂-8, CeO₂/TiO₂-4, and CeO₂/TiO₂-2, and compared the photoactivity of the samples with the 3D ordered macroporous TiO₂ (3DOM) and the commercial TiO₂ (P25). The outcomes demonstrated that the CeO₂/TiO₂-2, CeO₂/TiO₂-4 and CeO₂/TiO₂-8 composites had higher photoactivity than the TiO₂ and P25 samples, showing that the synergetic effect of TiO₂ and CeO₂ increased the photocatalytic efficiency. The CeO₂ sample showed the lower CO production amount. The best photocatalytic performance was obtained with the sample CeO₂/TiO₂-4. However, the amount of CO decreased with the increase in the CeO₂ loading amount (>4), showing that the amounts of CeO₂ nanolayers have optimal value. The composite sample with the higher amount of CeO₂, CeO₂/TiO₂-16, showed lower performance than the 3DOM TiO₂ and P25 samples, which can be explained due to the fact that the CeO₂ sample almost did not have photocatalytic activity for this reaction condition, and this can be the possible reason for the lower photocatalytic activity of this sample. The authors proposed a type-II photocatalytic mechanism for the CO₂ photoreduction using the CeO₂/TiO₂ composite, shown in Table 3. The increase in photoactivities during the photocatalytic reduction of CO₂ under Vis irradiation is due to the synergistic effect of the
heterojunction between CeO$_2$ and TiO$_2$ and photonic crystals. They concluded that the heterojunction between CeO$_2$ and TiO$_2$ increases the charge carriers separation, and the absorption efficiency of solar irradiation can be enhanced due to the slow light effect of the 3D ordered macroporous structure and the ordered macroporous facilitates the diffusion of the reactants [36].

Zhao et al. [37] investigated the effect of the TiO$_2$ polymorph phases, brookite, anatase, and rutile on the CeO$_2$/TiO$_2$ composites efficiency for the photocatalytic reduction for CO$_2$. They prepared CeO$_2$/TiO$_2$ composite using anatase, brookite and rutile, identified as A-TiCe, B-TiCe and R-TiCe, respectively. The results showed that the higher amount of CO yield produced was achieved using the sample rutile TiO$_2$/CeO$_2$ (R-TiCe). This enhancement in CO$_2$ photoreduction using the rutile TiO$_2$/CeO$_2$ sample was justified due to the formation of Ti defects at the CeO$_2$-rutile interfaces that improves the energy-band structure of rutile, facilitating the e$^-$/h$^+$ pairs’ separation. To go further, the authors prepared samples of rutile TiO$_2$/CeO$_2$ with different mass ratios of CeO$_2$/TiO$_2$, with CeO$_2$ 5.9, 12.9 and 24.3 wt.%, obtaining the samples, R-TiCe$_{0.05}$, R-TiCe$_{0.1}$, R-TiCe$_{0.2}$, respectively. They compared the activity of these rutile TiO$_2$/CeO$_2$ composites with the rutile TiO$_2$, CeO$_2$ and P25. The CeO$_2$ had the lower photocatalytic activity. The best photocatalyst for the CO$_2$ photoreduction was the R-TiCe$_{0.1}$ with the yield of CO. This result can be explained once the activity of CeO$_2$ is markedly lower when compared with the TiO$_2$, suggesting that in the CeO$_2$/TiO$_2$ composites, the TiO$_2$ is the principal active composition, and CeO$_2$ acts as a promoter [37].

Wang et al. [38] synthesized CeO$_2$/TiO$_2$ samples with CeO$_2$ 40, 20 and 10 wt.%, identified as 0.4 CeO$_2$/TiO$_2$, 0.2 CeO$_2$/TiO$_2$ and 0.1 CeO$_2$/TiO$_2$, respectively. The activity of the CeO$_2$/TiO$_2$ composites was compared with the CeO$_2$ and TiO$_2$ samples. Comparing all the samples, the best photocatalyst was the 0.2 CeO$_2$/TiO$_2$. Furthermore, they observed that the CeO$_2$/TiO$_2$ composites’ photoactivity enhances with the higher CeO$_2$ amount and reaches a maximum at 20 wt.% CeO$_2$ content (sample 0.2 CeO$_2$/TiO$_2$), since for the sample with higher CeO$_2$ content, the photocatalytic activity decreased. TiO$_2$ is the principal active composition, while CeO$_2$ acts as a promoter in the CeO$_2$/TiO$_2$ composites. CeO$_2$ content is the dominant factor on the enhancement of CO$_2$ photoreduction under simulated sunlight illumination. This work showed that CeO$_2$ extends the light absorption of the CeO$_2$/TiO$_2$ composite to the Vis range and enhances the e$^-$/h$^+$ separation, due to the presence of Ce$^{3+}$ [38].

2.3. CuO/TiO$_2$

Copper oxide, CuO, is a p-type semiconductor nanomaterial with a bandgap between 1.2 and 1.9 eV, among this narrow direct bandgap. This material has various properties, such as high electrical conductivity, good semiconducting nature, thermal stability, low toxicity and low cost. The bandgap of CuO should favor the Vis light absorption and enhance the photoactivity [41,67,68]. CuO has been used as a photocatalyst for the CO$_2$ photocatalytic conversion to solar fuels [69,70]. CuO exhibits spontaneous CO$_2$ adsorption ($\Delta H = -45$ kJ mol$^{-1}$) in comparison with TiO$_2$. The energy levels of the CO$_2$-adsorbed species, such as $\cdot$O-Cu-$\cdot$O-$\cdot$, can lead to an improvement in the visible-light absorption and efficient separation of electrons and holes that favors the photocatalytic activity of CuO [69,71]. Moreover, CuO presents selectivity to the formation of value-added solar fuels, such as CH$_3$OH and CH$_4$ in the photocatalytic CO$_2$ reduction [72]. For the above reasons, CuO/TiO$_2$ photocatalysts with heterojunction were also studied for the CO$_2$ photocatalytic reduction. CO$_2$ photocatalytic reduction using CuO/TiO$_2$ heterojunction photocatalysts is tabulated in Table 4.
| Photocatalysts          | CO₂ Photoreduction Condition                                      | Yield of Products          | Type of Heterojunction | Ref. |
|------------------------|------------------------------------------------------------------|----------------------------|------------------------|------|
| CuO/TiO₂(AB)           | Impregnation method                                               | HCOOCH₂ = ~1800 μmol g⁻¹·h⁻¹ | -                      | [41] |
| 3 wt.% CuO/TiO₂        | Impregnation method                                               | methanol = 12.5 μmol g⁻¹·h⁻¹| -                      | [42] |
| 1.0CuO-TiO₂            | Stirring method followed by calcination                           | Methyl formate ~1600 μmol g⁻¹·h⁻¹| Z-scheme               | [39] |
| CuO loaded TiO₂        | Hydrothermal method                                               | 100% CO₂ conversion into CH₄ and CH₃OH after 2.5 h | Type-I                 | [43] |

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Zhao et al. successfully prepared CuO-incorporated TiO$_2$ photocatalysts by an impregnation method, to be used as photocatalysts for the CO$_2$ reduction into methyl formate in methanol [41]. They observed that the heterojunction photocatalyst CuO/TiO$_2$(AB) had higher methyl formate yield than the pristine photocatalysts. It was caused by its mixed-phase heterojunction structure and higher specific surface area, resulting in an effective separation, an enhanced UV-light response, and a smaller recombination rate of photogenerated electrons and holes. CuO/TiO$_2$(AB) also demonstrated sufficient stability. The methyl formate yield reproducibility was higher than 90% in cyclic runs [41]. The experimental conditions are resumed in Table 4.

Li et al. [42] dealt with CO$_2$ photocatalytic reduction to produce CH$_3$OH and C$_2$H$_5$OH over CuO-loaded titania powders suspended in H$_2$O with Na$_2$SO$_3$, which was the hole scavenger and promoted the formation of ethanol. The authors prepared four composites with a copper amount between 1 and 7 wt.% (7 wt.% CuO/TiO$_2$, 5 wt.% CuO/TiO$_2$, 3 wt.% CuO/TiO$_2$, and 1 wt.% CuO/TiO$_2$). They observed that yields of methanol and ethanol are enhanced with a CuO amount until 3 wt.%, and for the samples with 5 and 7 wt.%, the yields are decreased, being in this case 3 wt.%, the ideal amount of CuO loading. Loading of CuO enhances CH$_3$OH and C$_2$H$_5$OH yields due to the higher amount of active sites. Copper is an electron catcher and inhibits e$^{-}$/h$^+$ recombination. However, the samples with a higher amount of copper (>3 wt.% CuO) cannot further enhance the CH$_3$OH and C$_2$H$_5$OH yields due to the excess of CuO, which covers the surface of TiO$_2$, decreasing the TiO$_2$ photoexciting capacity, thereby reducing the photoactivity [42].

Another example of CuO and TiO$_2$ heterojunction was reported by Qin et al. [39]. They studied the photocatalytic reduction of carbon dioxide in CH$_3$OH to methyl formate in the presence of CuO–TiO$_2$ photocatalysts. The methanol was used as the hole scavenger, which can react with the photogenerated holes in the VB, and CO$_2$ was reduced by the e$^-$ in the VB. The authors prepared samples with 0.5, 1, 3 and 5 weight percentage of CuO and compared their photocatalytic activity with TiO$_2$. The coupling of TiO$_2$ with CuO led to the rapid increase in the photoactivity because TiO$_2$ and CuO created composite photocatalysts, and electron and hole recombination was reduced.

However, as mentioned above, these authors also concluded that higher CuO loading (>1.0%, in this case) decreases the photoactivity because of the CuO particles’ agglomeration. The most active photocatalyst was 1.0CuO–TiO$_2$ (1 wt.% of CuO). The authors concluded that the heterojunction between TiO$_2$ and CuO was the decisive parameter for enhancing the photoactivity of the samples [39].

Razali et al. [43] prepared p–n type CuO–TiO$_2$ nanotube samples with improved ability for carbon dioxide photoconversion into fuels. They concluded that the higher photocatalytic efficiency of CuO–TiO$_2$ photocatalyst is attributed to the restraint of e$^-$ photogeneration and h$^+$ recombination, as the p–n heterojunction between the CuO particles and TiO$_2$ nanotube facilitates the charge separation between electrons and holes, due to the presence of an electrostatic field at the junction. Electrons in the CB of CuO transfer into the CB of TiO$_2$, whereas holes in the VB of TiO$_2$ transfer to the VB of CuO. The charge transfers and separation between both semiconductors may prohibit the recombination of electrons and holes, thus increasing the photocatalytic performance of the CuO-loaded TiO$_2$ nanotube [43].

2.4. CdS/TiO$_2$

Cadmium sulfide (CdS) is a semiconductor material from the II–VI group with a direct bandgap of 2.4 eV [73,74]. CdS is used for carbon dioxide photocatalytic reduction under UV light irradiation [11,75]. This photocatalyst has ideal properties, such as the capability of converting light energy into chemical, optical, photophysical and photochemical energy [75]. However, this material has some disadvantages, such as fast e$^{-}$/h$^+$ recombination, and photocorrosion vulnerability in aqueous solution due to oxidation by photo-generated holes during photocatalytic reaction [73]. Nevertheless, the photocatalytic activity of this semiconductor can be enhanced, for instance, by doping with metal
elements or by the combination with other semiconductors [73]. To date, CdS is widely used in the TiO\textsubscript{2}/CdS coupled heterojunction to improve the photoelectron conversion efficiency of photocatalysis and solar cell [74]. TiO\textsubscript{2}/CdS combination is reported as the one of the most representative hybrid semiconductors, once the valence and conduction bands of the CdS are appropriately located in relation to those of TiO\textsubscript{2} for higher charge separation, and also CdS can absorb a main part of visible light, as it is possible to use sunlight [44,76]. CO\textsubscript{2} photocatalytic reduction using CdS/TiO\textsubscript{2} heterojunction photocatalysts is tabulated in Table 5.

Park et al. [44] reported the photocatalytic conversion of CO\textsubscript{2} to CH\textsubscript{4} in the presence of TiO\textsubscript{2}/CdS in an isopropanol (IPA) solution under UV-Vis and Vis light irradiation. IPA is frequently used as a sacrificial e\textsuperscript{−} donor, such as an h\textsuperscript{+} scavenger. The authors prepared three TiO\textsubscript{2}/CdS composites, TiO\textsubscript{2}/CdS-5, TiO\textsubscript{2}/CdS-3 and TiO\textsubscript{2}/CdS-1, with varied amounts of loaded CdS to TiO\textsubscript{2}, approximately 33.7%, 23.6%, and 11.4%, respectively. However, they did not observe a significant difference on the obtained yields with the CdS amount on the TiO\textsubscript{2}, so they only reported the results obtained using the sample TiO\textsubscript{2}/CdS-3 as a photocatalyst for the CO\textsubscript{2} photoreduction. The authors analyzed the H\textsubscript{2} evolution and the production of CO and CH\textsubscript{4}, using Ar or CO\textsubscript{2} gas to purge (before irradiation) the aqueous TiO\textsubscript{2} and TiO\textsubscript{2}/CdS suspensions with isopropanol.

During the H\textsubscript{2} evolution, the results showed that using Ar-purged gas, the TiO\textsubscript{2}/CdS composite sample had better photocatalytic activity in comparison with the pristine TiO\textsubscript{2}. As expected, the production of H\textsubscript{2} in the Ar atmosphere was higher than in the CO\textsubscript{2} atmosphere, due to the competition for electrons. In contrast, for the CO production, it was observed that using CO\textsubscript{2}-purged gas, the TiO\textsubscript{2}/CdS composite sample had better photocatalytic activity in comparison with the pristine TiO\textsubscript{2}. This result was observed due to the better adsorption of CO\textsubscript{2} on CdS, as well as the increased charge carrier separation and transfer on the TiO\textsubscript{2}/CdS composite sample.

Regarding the CH\textsubscript{4} production, the results showed that regardless of the purge gas used (Ar or CO\textsubscript{2}), the TiO\textsubscript{2}/CdS composite sample had higher catalytic activity when compared with the TiO\textsubscript{2} sample. It is well known that CdS-modified TiO\textsubscript{2} is more active than pure TiO\textsubscript{2} for the formation of CH\textsubscript{4}. However, in this case, some part of the CH\textsubscript{4} obtained was formed due to the presence of IPA, both making a contribution to the observed CH\textsubscript{4} yields. Furthermore, the authors did not discard the idea that the presence of hydrocarbon contaminants during the preparation of the catalyst can be considered for a fraction of the obtained yields.

The authors also investigated the photoactivity of the TiO\textsubscript{2}/CdS sample (in CO\textsubscript{2}-purged gas) under Vis light irradiation. In this case, only the CdS photocatalyst was capable of excitation, and no significant differences on the CH\textsubscript{4} production were obtained using UV-vis and visible light irradiation, suggesting that the CdS plays a significant role in CO\textsubscript{2} fixation and in photocatalyzing the transference of multi-electrons to CO\textsubscript{2}.

With this work, the authors concluded that the presence of CdS on TiO\textsubscript{2} enhanced the production rate of CH\textsubscript{4} and enhanced the total CH\textsubscript{4} yields. They reported that this enhancement can be ascribed to the easy transference of e\textsuperscript{−} from the CdS to surface-bound CO\textsubscript{2}, resulting in to the formation of *CO\textsubscript{2}− that binds to the positively charged surface of CdS, and also due to the surface-bound bicarbonate geometry that increases the production of CH\textsubscript{4} due to smaller energy barriers in comparison with the linear O=C=O molecule [44].
| Photocatalysts          | CO₂ Photoreduction Condition | Yield of Products | Type of Heterojunction | Ref. |
|------------------------|------------------------------|-------------------|------------------------|------|
| TiO₂/CdS-3 Conventional hydrothermal technique | Ar or CO₂ (both 99.99%) for 1 h, and aqueous isopropanol solution (1.0 M, 100 mL) | methane = −18 µmol (after 10 h) CO = −2.5 µmol (after 10 h) | Type-II | * [44] |
| TiO₂/CdS Ionic layer adsorption and reaction (SILAR) method | CO₂ and H₂O vapor (from 84 mg of NaHCO₃ and 0.3 mL of HCl solution (4 M)) | 11.9 mmol h⁻¹ m⁻² for CH₄ production | Z-scheme | † [45] |
| CdS-TiO₂-8 Hydrothermal method | CO₂ and 10 mL cyclohexanol | cyclohexyl formate = 20.2 µmol g⁻¹ h⁻¹ cyclohexanone = 20 µmol g⁻¹ h⁻¹ | Z-Scheme | † [46] |
| CdS-TiO₂ S3 (45%) Hydrothermal method | N₂ and CO₂ | Under UV-vis irradiation: CO = −15.5 µmol g⁻¹ h⁻¹ CH₄ = −3.0 µmol g⁻¹ h⁻¹ after 8 h Under visible light irradiation: CO = −10.3 µmol g⁻¹ h⁻¹ CH₄ = −1.5 µmol g⁻¹ h⁻¹ | Type-II | ¥ [47] |

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Low et al. [45] described a direct Z-scheme TiO$_2$/CdS composite with high efficiency for the photocatalytic reduction of CO$_2$. They compared the photocatalytic activity of the TiO$_2$/CdS composite with the TiO$_2$, CdS and commercial P25 samples. The TiO$_2$/CdS composite formed 3.5-, 5.4-, and 6.3-times higher amounts of CH$_4$ than the TiO$_2$, CdS and commercial P25, respectively. They compared the type II and direct Z-scheme possibility for the mechanism of their TiO$_2$/CdS composites during activation. With a simple test of the *OH production (using coumarin to trap *OH and produce fluorescent products, it is possible to analyze by fluorescence spectroscopy) they concluded that it was possible to produce this radical. On the other hand, using the CdS photocatalyst was not obtained, due to the position of the VB (around 1.8 V) being lower than the potential of this reaction ($E^0$(OH$^-$/*OH) = 2.4 V). So, the *OH was formed on the TiO$_2$ side of the composite, following the direct Z-scheme mechanism of the charge-transfer process, as shown in the schematic illustration in Table 5. The enhanced performance obtained in the presence of the TiO$_2$/CdS composite can be explained due to the e$^-$/h$^+$ availability (according to the enhanced photocurrent for this sample), due to the direct Z-scheme heterojunction [45].

Song et al. [46] prepared four CdS–TiO$_2$ samples with various molar ratios, named CdS–TiO$_2$-X (X is molar ratios of TiO$_2$/CdS: CdS–TiO$_2$-10, CdS–TiO$_2$-9, CdS–TiO$_2$-8, and CdS–TiO$_2$-6. All composites had higher activity for the CO$_2$ photoreduction than CdS and TiO$_2$. This can be explained due to the interaction between TiO$_2$ and CdS that improved the photocatalytic reduction capacity of CO$_2$.

They observed that the increase in the CdS amount in the composites until 8:1 increased the efficiency, obtaining the CdS–TiO$_2$-8, optimal photoactivity for the production of cyclohexyl formate (CF) and cyclohexanone (CH). However, for CdS content higher than 8:1 TiO$_2$/CdS molar ratios, a decrease in the photocatalytic activity was observed, indicating that a high amount of CdS in the TiO$_2$ photocatalyst decreases the photogenerated e$^-$ on the TiO$_2$ and then leads to a smaller photocatalytic activity. The exactly 1 mole of excited TiO$_2$ has to correspond to 1 mole of excited CdS; otherwise, the exceeded e$^-$ or h$^+$ recombine to decrease the reaction rates. In addition, for the higher than 8:1 TiO$_2$/CdS molar ratios, there were difficulties in the light absorbance once the higher amount of CdS aggregated on the surface of the TiO$_2$ nanosheets, which hampered the absorption of light by the TiO$_2$. Furthermore, they concluded that the CO$_2$ absorbed in cyclohexanol can be decreased to CF, and the cyclohexanol oxidized into CH on the conduction band and valence band of the TiO$_2$/CdS photocatalyst, respectively (as can be seen in the scheme of Table 5) [46].

Ahmad Beigi et al. [47] reported the preparation of CdS/TiO$_2$ nanocomposites for the photocatalytic reduction of CO$_2$ to CO and CH$_4$ under UV-vis and visible light irradiation. For this study, four CdS/TiO$_2$ samples were synthesized with different weight ratios of CdS in TiO$_2$: S1 (9%), S2 (23%), S3 (45%) and S4 (74%). All CdS/TiO$_2$ nanocomposites had higher photocatalytic activity than the TiO$_2$ and CdS samples. The CO was the majoritarian product of this reduction reaction. The presence of CdS greatly improved the photocatalytic efficiency of the TiO$_2$, and the best performance was achieved using the composite CdS/TiO$_2$ S3 (45%), which was the optimal ratio of CdS/TiO$_2$ for CO$_2$ photoreduction. The enhancement used the CdS/TiO$_2$ S3 (45%) composite, due to the large specific surface area and low crystal size of this sample.

As in the works reported above, the ratio of CdS in the composites was crucial to the photocatalytic performance of the composites. In this case, the authors also reported that the crystal size and specific surface area were the parameters that influenced the performance of these composites for the CO$_2$ reduction. Therefore, a certain amount of CdS can enhance the TiO$_2$ photocatalytic activity, and the porous structure of this CdS/TiO$_2$ composite can have reacting sites for electrons transference to the reactant and avoid the recombination of the e$^-$/h$^+$ [47].

### 2.5. MoS$_2$/TiO$_2$

Molybdenum disulfide, MoS$_2$, is a typical representative of two-dimensional (2D) transition metal chalcogenides (transition metal dichalcogenides—TMDs) [77]. Any one layer
of MoS$_2$ contains three atomic layers (S–Mo–S) stacked together [78]. This material is used as a substitute for noble metal co-catalysts, due to its properties, such as high activity, low cost, excellent chemical stability and abundance, and the band gap being around 1.3 to 1.9 eV [79]. Coupling TiO$_2$ with MoS$_2$ [49,80] leads to the creation of a heterojunction structure, which can speed up the electron transfer and reduce the photogenerated electrons and holes recombination. This heterojunction composite was recently studied for application on photocatalytic systems. MoS$_2$/TiO$_2$ composites were widely investigated as photocatalysts for photocatalytic degradation, hydrogen evolution, and CO$_2$ reduction; with this combination, the reduction of the electron/hole recombination should be possible, and also the presence of MoS$_2$ provides large catalytically active sites for photocatalytic progress [79]. CO$_2$ photocatalytic reduction using MoS$_2$/TiO$_2$ heterojunction photocatalysts is tabulated in Table 6.

Peng-yao Jia et al. in 2019 [49] synthesized the MoS$_2$/TiO$_2$ heterojunction composites with different mass ratios of MoS$_2$, 0, 5, 10 and 15 wt.%, obtaining the samples of TiO$_2$, 5 wt.% MoS$_2$/TiO$_2$, 10 wt.% MoS$_2$/TiO$_2$, and 15 wt.% MoS$_2$/TiO$_2$, respectively. The obtained results showed that the 10% MoS$_2$/TiO$_2$ sample had higher photocatalytic activity for the photoreduction of CO$_2$, obtaining higher amounts of CO and CH$_4$ than the other composite materials. The achieved yields of CH$_4$ and CO on the 10% MoS$_2$/TiO$_2$ heterojunction photocatalyst were approximately 5 times and 16 times higher than for pure TiO$_2$ (P25). This result can be explained due to the lower band gap energy of this material, and also this material showed the lowest e$^-$/h$^+$ recombination by PL characterization; the photocurrent characterization indicates that this sample had more enhancement in e$^-$ and h$^+$ separation. The authors proposed a type-II heterojunction mechanism for this sample as can be seen in Table 6. Once the CB edge potential of MoS$_2$ ($-0.93$ V) is more negative than that of TiO$_2$ ($-0.55$ V), the migration of e$^-$ from the surface of MoS$_2$ to accumulate in the TiO$_2$ is possible, due to the contact in the interface [49].

Xu et al. [50] described the preparation of 1D/2D TiO$_2$/MoS$_2$ nanostructured photocatalysts for increased photocatalytic CO$_2$ reduction. The authors prepared different TiO$_2$/MoS$_2$ samples, with 1%, 5%, 7.5%, 10%, 15% and 25% of MoS$_2$, labelled as TMx, where T and M are TiO$_2$ and MoS$_2$, respectively, and x denotes the mol.% of MoS$_2$ to TiO$_2$.

They observed that the formation rate of CH$_4$ and CH$_3$OH was markedly increased with higher MoS$_2$ loading. The maximum value for the CH$_4$ and CH$_3$OH yields was reached for the TM10 sample. On the other side, only CH$_3$OH was observed as the product in the presence of pure TiO$_2$.

The authors concluded that the enhanced photocatalytic efficiency of TM10 is attributed to the increased light absorption, implying that more optical energy is absorbed after hybridization; the increased specific surface area nominates a higher amount of accessible reactive sites between TiO$_2$/MoS$_2$ and CO$_2$ molecules; there is a higher CO$_2$ adsorption capacity since CO$_2$ adsorption is the beginning step for the next reduction processes; and there is enhanced charge separation, owing to the presence of MoS$_2$ nanosheets as a cophotocatalyst [50].

In the TiO$_2$/MoS$_2$ samples, the photoinduced e$^-$ in TiO$_2$ transfers to MoS$_2$, reaching more efficient electron–hole separation. Thus, the number of catalytically active e$^-$ is significantly improved over pure TiO$_2$, favoring the 8 e$^-$ reaction for producing CH$_4$. For that reason, the TMx showed higher photocatalytic CO$_2$ reduction activity and better selectivity of CH$_4$ than the pure TiO$_2$ photocatalyst. However, the next increasing amount of MoS$_2$ resulted in a decrease in the photocatalytic activity (e.g., TM25 and TM15), probably because of the severe charge carrier recombination and the shielding effects toward light absorption or the transfer of electrons, owing to the presence of a high amount of MoS$_2$. 

Table 6. CO$_2$ photoreduction using MoS$_2$/TiO$_2$ heterojunction photocatalysts.

| Photocatalysts | CO$_2$ Photoreduction Condition | Yield of Products | Type of Heterojunction | Ref. |
|----------------|---------------------------------|-------------------|------------------------|------|
| Type          | Prepared                         | Reaction Mixture  | Light Source           | Conditions              | Products | Type                        | |
| 10% MoS$_2$/TiO$_2$ | Calcined at 300 °C for 4 h with argon shielding gas | 100 mL deionized H$_2$O which was preprocessed for 30 min with CO$_2$ (99.99%) of 100 kPa | Xe-arc lamp 300 W acting | 500 cm$^3$ cylindrical reactor Photocatalyst concentration in 0.5 g L$^{-1}$ | CO = 268.97 µmol g$^{-1}$ cat CH$_4$ = 49.93 µmol g$^{-1}$ cat after 6 h | Type-II | * [49] |
| 10% MoS$_2$/TiO$_2$ | In situ growing MoS$_2$ nanosheets onto TiO$_2$ nanofibers by hydrothermal method | CO$_2$ and H$_2$O vapor were in situ generated by the reaction of NaHCO$_3$ (0.12 g) and H$_2$SO$_4$ aqueous solution (0.25 mL, 2 M) | 350 W Xe lamp | 200 mL homemade Pyrex reactor Photocatalyst concentration in 0.25 g L$^{-1}$ | CH$_4$ = 2.86 µmol g$^{-1}$ h$^{-1}$ CH$_3$OH = 2.55 µmol g$^{-1}$ h$^{-1}$ | Type-II | ‡ [50] |
| 0.5 wt% MoS$_2$/TiO$_2$ | Hydrothermal method | 200 mL of 1 M NaHCO$_3$ solution and pure CO$_2$ | 300 W Xenon arc lamp. airtight quartz glass reactor Photocatalyst concentration in 0.5 g L$^{-1}$ | CH$_3$OH = 10.6 µmol g$^{-1}$ h$^{-1}$ | - | |

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In this study, the author also analyzed the stability of the TM10 catalyst in consecutive reutilizations and concluded that TM10 is stable without loss of photoactivity for four cycles.

Test with an isotope tracer confirmed that the products of CO\textsubscript{2} photocatalytic reduction solely originated from the CO\textsubscript{2} source. The DFT calculation demonstrated that TiO\textsubscript{2} has a higher work function than MoS\textsubscript{2}, resulting in electrons transfer from MoS\textsubscript{2} to TiO\textsubscript{2} upon their contact, which supports the charge carrier separation of upon photocatalysis. Moreover, the hybridization with MoS\textsubscript{2} increases light harvesting and enhances the CO\textsubscript{2} adsorption of TiO\textsubscript{2}, further contributing to the superior photocatalytic efficiency of the TiO\textsubscript{2}/MoS\textsubscript{2} hybrid [50].

Tu et al. [51] described the preparation of two-dimensional MoS\textsubscript{2}–TiO\textsubscript{2} hybrid nanojunctions, for the CO\textsubscript{2} photocatalytic reduction to CH\textsubscript{3}OH. They prepared MoS\textsubscript{2}/TiO\textsubscript{2} photocatalysts with 3, 2, 1, and 0.5 wt.% contents of MoS\textsubscript{2}.

All samples proved photocatalytic activity for CO\textsubscript{2} photoreduction into CH\textsubscript{3}OH, the 0.5 wt.% MoS\textsubscript{2}/TiO\textsubscript{2} sample being the one with the best photocatalytic performance for this reaction. Using this sample, CH\textsubscript{3}OH production was almost three times higher than using pure TiO\textsubscript{2}. However, for the samples with higher MoS\textsubscript{2} content (1, 2, and 3 wt.%) a gradual decrease in the photocatalytic activity was obtained. This occurs due to the fact that the photons in the photocatalytic system are absorbed by the excess of black MoS\textsubscript{2} nanosheets, and probably decrease the light intensity through shielding the light reached on the TiO\textsubscript{2} surface (i.e., “shielding effect”).

It was found that the two-dimensional MoS\textsubscript{2}/TiO\textsubscript{2} hybrid composites presented high photocatalytic activity for CO\textsubscript{2} photoreduction. They concluded that loaded MoS\textsubscript{2} nanosheets minimize the charge carrier recombination and enhance the conversion performance of the CO\textsubscript{2} photoreduction into CH\textsubscript{3}OH due to the e\textsuperscript{−} transfer from TiO\textsubscript{2} to MoS\textsubscript{2} [51].

2.6. Other Semiconductors

In this section, studies on the CO\textsubscript{2} photoreduction using composite materials with heterojunction with TiO\textsubscript{2} not so often used until now are shown. CO\textsubscript{2} photocatalytic reduction using GaP/TiO\textsubscript{2}, CaTiO\textsubscript{3}/TiO\textsubscript{2} and FeTiO\textsubscript{3}/TiO\textsubscript{2} heterojunction photocatalysts are tabulated in Table 7.

2.6.1. GaP/TiO\textsubscript{2}

Gallium phosphide, GaP, is a semiconductor material with an indirect band gap of 2.3 eV, insoluble in water. This semiconductor is not often used as a photocatalyst due to the low oxidizing power of its VB; however, the conduction band (CB) position allows the CO\textsubscript{2} reduction once it is 1.26 V more negative than that of CO\textsubscript{2}/CH\textsubscript{4} (\(E^0 = -0.24\) V) and 0.97 V more negative than CO\textsubscript{2}/CO (\(E^0 = -0.53\) V), as can be seen in the reactions from Table 1.

In 1978, Halmann [81] used GaP for the photoelectrochemical reduction of CO\textsubscript{2}. In this case, GaP was used in the liquid junction of solar cells, and the obtained products were formic acid, formaldehyde and methanol [52,81]. Furthermore, recently, Barton et al. also used GaP and found that a highly selective CO\textsubscript{2} photoreduction to CH\textsubscript{3}OH occurred when a GaP electrode with pyridine was used. In this case, pyridine served as a cocatalyst [52,82]. Regardless of the fact that electrons from the GaP conduction band can reduce CO\textsubscript{2} to methane, we need to look at the oxidation reaction as well. For example, oxygen, water vapor is chosen as the hole trap (oxidation step). In this case, oxygen cannot be used as a hole trap because the GaP valence band (\(E^0 = 0.80\) V) does not have sufficient potential for water oxidation (\(E^0 = 0.82\) V). Therefore, the pristine GaP cannot be used for the CO\textsubscript{2} photocatalytic reduction.
Table 7. CO$_2$ photoreduction using GaP/TiO$_2$, CaTiO$_3$/TiO$_2$ and FeTiO$_3$/TiO$_2$ heterojunction photocatalysts.

| Photocatalysts | Prepared | Reaction Mixture | Light Source | Conditions | Yield of Products | Type of Heterojunction | Ref. |
|----------------|----------|------------------|--------------|------------|-------------------|------------------------|------|
| 1:10 GaP/TiO$_2$ | Mechanically milling of Commercial TiO$_2$ Evonik P25 and GaP Aldrich powders | CO$_2$ and water | 1500 W high pressure Xe lamp | gas–solid Pyrex batch photoreactor of cylindrical shape (V = 100 mL, Φ = 94 mm, height = 15 mm) Photocatalyst concentration in 3 g L$^{-1}$ | CH$_4$ = 118.18 μM g$^{-1}$ after 10 h | Z-scheme | [52] |
| 20% FeTiO$_3$/TiO$_2$ | Hydrothermal method | 30 mL distilled water containing sodium bicarbonate (NaHCO$_3$, 0.08 M) | 500 W high-pressure Xe lamp | quartz reaction vessel, connected to a gas chromatograph. Photocatalyst concentration in 1.7 g L$^{-1}$ | CH$_3$OH = 0.462 μmol g$^{-1}$ h$^{-1}$ under UV-vis irradiation and CH$_3$OH = 0.432 μmol g$^{-1}$ h$^{-1}$ under visible light irradiation. | - | [53] |
| 13.4% CaTiO$_3$/TiO$_2$ | In situ hydrothermal method | CO$_2$ and water | 300 W Xe lamp | Quartz tube reactor, with 43 mL volume Photocatalyst concentration in 0.23 g L$^{-1}$ | CO = 11.72 μmol g$^{-1}$ h$^{-1}$ | Z-scheme | [54] |

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In line with this, Giuseppe Marci et al. [52], for the first time, evaluated the GaP/TiO$_2$ composites for the photocatalytic reduction of carbon dioxide. The suitable position of VB and CB of the semiconductors not only allows for heterojunction photocatalysts (GaP/TiO$_2$) to have efficient electron–hole separation, but also enables both H$_2$O oxidation and CO$_2$ reduction.

Giuseppe Marci et al. [52] reported GaP/TiO$_2$ photocatalysts with significant efficiency during the photocatalytic reduction of carbon dioxide to the formation of methane. The researchers concluded that decreasing the mass ratio of the GaP:TiO$_2$ enhances the photocatalytic efficiency of the photocatalyst, and the highest efficiency was observed in the presence of photocatalysts with a 1:10 mass ratio. The photocatalytic effectiveness of the photocatalysts was connected with the band structures of the semiconductors and also with the efficient electron–hole transfer between GaP and TiO$_2$ in the heterojunction photocatalysts.

2.6.2. FeTiO$_3$/TiO$_2$

Another interesting alternative to improve the TiO$_2$ photocatalytic reduction of CO$_2$ is the combination with ternary oxides, such as ilmenite (FeTiO$_3$) and perovskite (CaTiO$_3$); these heterojunction composite materials have not been studied very much for the photocatalytic reduction of CO$_2$. However, the works reported by Truong et al. [53] and Lin et al. [54] showed that FeTiO$_3$/TiO$_2$ and CaTiO$_3$/TiO$_2$, respectively, are promising materials for this photocatalytic reaction.

Ilmenite (FeTiO$_3$) is a semiconductor material with a band gap energy between 2.59 and 2.90 eV. This is one of the most abundant minerals used as raw material for the production of TiO$_2$ and Ti. FeTiO$_3$ has been studied by several researchers, due to its optic, semiconductive and magnetic properties, low-cost and high abundance (as natural ilmenite), being an alternative semiconductor for photoactivated processes [83–88]. This semiconductor has been used for the formation of hetero-interfaces, with other different semiconductors, such as p–n junctions and Schottky contacts for effective carrier separation [89]. Recently, it was reported the high efficiency of FeTiO$_3$ as a photocatalyst for hydrogen production [83]. Furthermore, several works have been reported with the preparation and utilization of FeTiO$_3$-TiO$_2$ composites as photocatalysts for the degradation of organic pollutants, showing that this combination improves the photocatalytic activity [84,85,90,91].

Truong et al. [53] showed the photocatalytic reduction of CO$_2$ using the FeTiO$_3$/TiO$_2$ photocatalyst. The authors reported the preparation of a heterojunction sample of FeTiO$_3$/TiO$_2$ with various Fe/Ti mole ratios of 70%, 50%, 20%, and 10% [53]. All FeTiO$_3$/TiO$_2$ composites had a significantly higher photocatalytic activity for the carbon dioxide reduction under both radiation sources (UV–Vis and visible light) in comparison with the TiO$_2$ and P25 samples. This can be explained due to the heterojunction effect between the two semiconductors, and also the higher activity in the visible light due to the combination of TiO$_2$ with FeTiO$_3$. In the FeTiO$_3$/TiO$_2$ composites, the $e^-$ in the valence band of TiO$_2$ transfer to FeTiO$_3$ VB, while the $h^+$ are subsequently created in TiO$_2$ CB. Furthermore, the $e^-$/h$^+$ are photogenerated, owing to the narrow bandgap of FeTiO$_3$ [53,91]. The obtained results showed that 20% FeTiO$_3$/TiO$_2$ sample had the best photocatalytic activity. In cases with a higher amount of FeTiO$_3$ (50% and 70%), the CH$_3$OH production decreased. This was explained by the smaller surface area, and also the high metal amount in FeTiO$_3$/TiO$_2$, which can represent recombination centers, resulting in reduced photocatalytic efficiency. The enhanced photocactivity along with an increasing amount of FeTiO$_3$ is reasonable, due to the higher number of active sites for the carbonate species reduction. The optimal FeTiO$_3$ amount for the highest photocatalytic efficiency is 20 wt.%. The authors concluded with this study that the unique band structure, the heterojunction effect of two materials, and the FeTiO$_3$ narrow bandgap were responsible for the significant photocatalytic effectiveness on selective CH$_3$OH production during CO$_2$ photoreduction [53].

2.6.3. CaTiO$_3$/TiO$_2$

CaTiO$_3$ is a titanium-based perovskite-type oxide, and an n-type semiconductor with a large band gap between 3.0 and 3.5 eV. This is an alkaline earth metal titanate that is
non-toxic, with chemical stability, optical properties, a low cost and an eco-friendly nature. Currently, it is being used for several applications, such as electronic devices, photocatalytic degradation of dyes, water splitting for H\textsubscript{2} production and CO\textsubscript{2} reduction [92]. CaTiO\textsubscript{3} has been studied for the preparation of heterostructured photocatalysts systems to improve their photocatalytic activity, in order to promote separation and photogenerated charge carrier transportation, also leading to the improvement in their visible light response. For example, coupling CaTiO\textsubscript{3} with TiO\textsubscript{2} was studied for organic pollutants’ photodegradation [93]; however, for the CO\textsubscript{2} reduction, only one study was reported to date.

Lin et al. [54] synthesized four CaTiO\textsubscript{3}/TiO\textsubscript{2} composite samples with different amounts of TiO\textsubscript{2}, 0.4, 0.3, 0.2 and 0.1 g, obtaining samples named 8.6\%CaTiO\textsubscript{3}/TiO\textsubscript{2}, 13.4\%CaTiO\textsubscript{3}/TiO\textsubscript{2}, 24.2\%CaTiO\textsubscript{3}/TiO\textsubscript{2} and 66.7\%CaTiO\textsubscript{3}/TiO\textsubscript{2}, respectively, with the weight contents of CaTiO\textsubscript{3} obtained by XRD quantification.

The activity of these four CaTiO\textsubscript{3}/TiO\textsubscript{2} had higher photoactivity for the CO\textsubscript{2} photoreduction than the TiO\textsubscript{2} and P25 samples. The best sample for this reduction reaction was 13.4\%CaTiO\textsubscript{3}/TiO\textsubscript{2}, being that the photocatalytic activity of this sample was six times higher than the TiO\textsubscript{2}. The results also showed that the CaTiO\textsubscript{3} and TiO\textsubscript{2} ratio influenced the photocatalytic activity efficiency for the CO\textsubscript{2} photoreduction, i.e., the increase in CaTiO\textsubscript{3} content above 13.4\%CaTiO\textsubscript{3}/TiO\textsubscript{2} decreased the CO evolution. The authors reported that when an excess of CaTiO\textsubscript{3} content was introduced, a nanocubic morphology was obtained instead of a nanosheets morphology, and also the specific surface area decreased, being the reason for the decrease in the CO production. The authors concluded that the enhancement in the CaTiO\textsubscript{3}/TiO\textsubscript{2} composites catalytic activity for CO\textsubscript{2} photoreduction was attributed to the similar crystal structures and the matched band structures of the CaTiO\textsubscript{3}/TiO\textsubscript{2} heterojunction photocatalysts that simplified the photogenerated electron–hole separation, as well as the increased surface basicity of the CaTiO\textsubscript{3}/TiO\textsubscript{2} samples that provided more abundant active sites for adsorption of CO\textsubscript{2} and, therefore, increased the photoreduction CO\textsubscript{2} [54].

2.7. Semiconductor-Covalent Organic Framework Z-Scheme Heterojunctions

The integration of covalent organic frameworks (COFs) with inorganic materials gives possibilities to develop new type of composite materials [94]. These materials have high surface areas and novel functionalities relevant to photocatalysis, chemical adsorption, and magnetic resonance imaging. The disadvantages of these materials associated with challenging, multi-step synthesis were overcome by Zhu et al. [94], who reported a one-pot synthesis approach, using a wide range of metal oxides to catalyze the synthesis of highly crystalline and porous COFs.

A series of COF semiconductor Z-scheme photocatalysts integrating semiconductors (TiO\textsubscript{2}, Bi\textsubscript{2}WO\textsubscript{6} and α-Fe\textsubscript{2}O\textsubscript{3}) with COFs (COF-316/318) were synthesized and characterized by Zhang et al. [95]. Prepared photocatalysts showed high photocatalytic CO\textsubscript{2} conversion to CO efficiency, with H\textsubscript{2}O as an electron donor in the gas–solid CO\textsubscript{2} reduction without additional photosensitizers and sacrificial agents. This is the first report of a covalent-bonded COF-inorganic semiconductor Z-scheme applied for artificial photosynthesis. The COF-318-TiO\textsubscript{2} Z-scheme heterojunction photocatalyst showed the highest CO production rate, which was about six times higher than the pure COF-318, and TiO\textsubscript{2} was also much higher than the physical mixture composites. Experiment studies and density functional theory (DFT) confirmed the efficient electron transfer from semiconductors to COFs by covalent coupling, resulting in the electrons being accumulated in cyano/pyridine of COF for the reduction of CO\textsubscript{2} and positive holes remaining in the semiconductor for the oxidation of H\textsubscript{2}O. This work found a new method to create a covalent bond linked organic–inorganic Z-scheme heterojunction and showed a new perspective in the field of photocatalysis.

3. Final Conclusions

Nowadays, energy depletion and environmental pollution is one of the most discussed topics. The photocatalytic reduction of carbon dioxide into valuable and clean fuels can
be one of the sustainable solutions to reduce carbon dioxide emissions. Although photo-catalytic CO$_2$ reduction has received unprecedented attention from scientists worldwide, its widespread use is limited due to the low selectivity, stability and especially the low efficiency of the photocatalytic system. The most studied photocatalyst in recent years is TiO$_2$ because it is cheap, non-toxic and environmentally friendly. Unfortunately, TiO$_2$ has some limitations, such as its activation, especially in the UV region, or the rapid recombination of generated electrons and holes. These imperfections can be tuned by doping TiO$_2$ with metals or non-metals or by creating TiO$_2$ heterojunction photocatalysts with other semiconductors.

In this review, TiO$_2$ heterojunction photocatalysts were discussed to further increase the photocatalytic efficiency of TiO$_2$ photocatalysts. In the last few years, several studies have been published on the preparation of TiO$_2$ heterojunction photocatalysts suitable for photocatalytic CO$_2$ reduction. Using these materials with the heterojunction, it was possible to improve the catalytic activity for the photoreduction of CO$_2$, due to the efficient electron transference in the interface, supporting the separation of the e$^-$/h$^+$ pairs and consequently reducing the e$^-$/h$^+$ recombination. In addition, the activity in the visible light range was improved because it was possible to utilize sunlight more effectively; there was higher adsorption of CO$_2$ due to the highly specific surface area; and there was an increase in selectivity specific CO$_2$ photoreduction products due to the contribution of the cocatalysts. In the case of heterojunction photocatalysts, there is always an optimal amount or ratio of semiconductors used. The use of the metal as a dopant TiO$_2$, which then forms a heterojunction with C$_3$N$_4$, also proved to be very advantageous.

Further research in this area should focus on the following aspects:

- To create heterojunction photocatalysts, it is essential to find materials that have the appropriate band structure for redox reactions, are active in the visible light region, and are stable.
- Efforts are underway to develop not too complex, efficient and effective methods for preparing heterojunction photocatalysts that could be produced in larger quantities. The most appropriate physicochemical properties of each semiconductor, such as the appropriate morphology, crystallite size, phase composition, etc., should be considered when developing preparation methods.
- The migration pathways of photogenerated electron–hole pairs need to be thoroughly studied. Heterojunction photocatalysts can have different arrangements (e.g., heterojunction type II or Z-scheme heterojunction) and, thus, different migration pathways for electron–hole separation, which need to be thoroughly studied and confirmed using advanced characterization techniques.
- To better understand the mechanism of migration pathways, knowledge from modeling methods or theoretical calculations should be used.

We hope that this review will encourage new approaches to the preparation of heterojunction photocatalysts, help optimize existing photocatalysts and create new efficient heterojunctions to achieve the higher efficiencies that are necessary for practical applications.

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References

1. Hannah, R.; Roser, M. CO2 and greenhouse gas emissions. Our World Data 2017. Available online: https://ourworldindata.org/co2-and-other-greenhouse-gas-emissions (accessed on 15 October 2021).

2. Lee, C.W.; Yang, K.D.; Nam, D.-H.; Jang, J.H.; Cho, N.H.; Im, S.W.; Nam, K.T. Defining a materials database for the design of copper binary alloy catalysts for electrochemical CO2 reduction. Adv. Mater. 2018, 30, 1704717. [CrossRef] [PubMed]

3. Appel, A.M.; Barr, J.E.; Bocarsly, A.B.; Dobek, H.; DuBois, D.L.; Dupuis, M.; Ferry, J.G.; Fujita, E.; Hille, R.; Kenis, P.J.A.; et al. Frontiers, Opportunities, and challenges in biochemical and chemical catalysis of CO2 fixation. Chem. Rev. 2013, 113, 6621–6658. [CrossRef]

4. Koçi, K.; Dang Van, H.; Edelmannová, M.; Reli, M.; Wu, J.C.S. Photocatalytic reduction of CO2 using Pt/C3N4 photocatalysts. Appl. Surf. Sci. 2020, 503, 144426. [CrossRef]

5. Habisreutinger, S.N.; Schmidt-Mende, L.; Stolarczyk, J.K. Photocatalytic reduction of CO2 on TiO2 and other semiconductors. Angew. Chem. Int. Ed. 2013, 52, 7372–7408. [CrossRef] [PubMed]

6. Hiragond, C.; Ali, S.; Sorcar, S.; In, S.-I. Hierarchical nanostructured photocatalysts for CO2 photoreduction. Catalysts 2019, 9, 370. [CrossRef]

7. Ziarati, A.; Badiei, A.; Grillo, R.; Burgi, T. 3D Yolk@Shell TiO2-x/LDH architecture: Tailored structure for visible light CO2 conversion. ACS Appl. Mater. Interfaces 2019, 11, 5903–5910. [CrossRef]

8. Nguyen, T.P.; Nguyen, D.L.T.; Nguyen, V.-H.; Le, T.-H.; Vo, D.-V.N.; Trinh, Q.T.; Bae, S.-R.; Chae, S.Y.; Kim, S.Y.; Le, Q.V. Recent advances in TiO2-based photocatalysts for reduction of CO2 to fuels. Nanomaterials 2020, 10, 337. [CrossRef]

9. Gao, Y.; Qian, K.; Xu, B.; Li, Z.; Zheng, J.; Zhao, S.; Ding, F.; Sun, Y.; Xu, Z. Recent advances in visible-light-driven conversion of CO2 by photocatalysts into fuels or value-added chemicals. Carbon Resour. Convers. 2020, 3, 46–59. [CrossRef]

10. Li, K.; Teng, C.; Wang, S.; Min, Q. Recent advances in TiO2-based heterojunctions for photocatalytic CO2 reduction with water oxidation: A Review. Front. Chem. 2021, 9, 637501. [CrossRef]

11. Inoue, T.; Fujishima, A.; Konishi, S.; Honda, K. Photocatalytic reduction of semiconductor powders. Nature 1979, 277, 637–638. [CrossRef]

12. Wei, L.; Yu, C.; Zhang, Q.; Liu, H.; Wang, Y. TiO2-based heterojunction photocatalysts for photocatalytic reduction of CO2 into solar fuels. J. Mater. Chem. 2018, 6, 22411–22436. [CrossRef]

13. Ohtani, B.; Handa, J.-i.; Nishimoto, S.-i.; Kagiya, T. Highly active semiconductor photocatalyst: Extra-fine crystallite of brookite TiO2 for redox reaction in aqueous propan-2-ol and/or silver sulfate solution. Chem. Phys. Lett. 1985, 120, 292–294. [CrossRef]

14. Li, Y.; Zhou, M.; Cheng, B.; Shao, Y. Recent advances in g-C3N4-based heterojunction photocatalysts. J. Mater. Sci. Technol. 2020, 56, 1–17. [CrossRef]

15. Liu, X.; Dang, R.; Dong, W.; Huang, X.; Tang, J.; Gao, H.; Wang, G. A sandwich-like heterostructure of TiO2 nanosheets with MIL-100(Fe): A platform for efficient visible-light-driven photocatalysis. Appl. Catal. B 2017, 209, 506–513. [CrossRef]

16. Xiong, Z.; Wang, H.; Xu, N.; Li, H.; Fang, B.; Zhao, Y.; Zhang, J.; Zheng, C. Photocatalytic reduction of CO2 on Pt2+/Pt0/TiO2 nanoparticles under UV/Vis light irradiation: A combination of Pt2+ doping and Pt nanoparticles deposition. Int. J. Hydrogen Energy 2015, 40, 10049–10062. [CrossRef]

17. Liu, X.; Dong, G.; Li, S.; Lu, G.; Bi, Y. Direct observation of charge separation on anatase TiO2 crystals with selectively etched [001] facets. J. Am. Chem. Soc. 2016, 138, 2917–2920. [CrossRef]

18. Low, J.; Yu, J.; Jaroniec, M.; Wageh, S.; Al-Ghamdi, A.A. Heterojunction photocatalysts. Adv. Mater. 2017, 29, 1601694. [CrossRef]

19. Low, J.; Yu, J.; Jiang, C. Design and fabrication of direct Z-scheme photocatalysts. In Interface Science and Technology; Yu, J., Jaroniec, M., Jiang, C., Eds.; Elsevier: Amsterdam, The Netherlands, 2020; Volume 31, pp. 193–229.

20. Bard, A.J. Photoelectrochemistry and heterogeneous photo-catalysis at semiconductors. J. Photochem. Photobiol. 1979, 10, 59–75. [CrossRef]

21. Tada, H.; Mitsui, T.; Kiyonaga, T.; Akita, T.; Tanaka, K. All-solid-state Z-scheme in CdS-Au-TiO2 three-component nanojunction system. Nat. Mater. 2006, 5, 782–786. [CrossRef]

22. Yu, J.; Wang, S.; Low, J.; Xiao, W. Enhanced photocatalytic performance of direct Z-scheme g-C3N4-TiO2 photocatalysts for the decomposition of formaldehyde in air. Phys. Chem. Chem. Phys. 2013, 15, 16883–16890. [CrossRef]

23. Yang, C.; Qin, J.; Xue, Z.; Ma, M.; Zhang, X.; Liu, R. Rational design of carbon-doped TiO2 modified g-C3N4 via in-situ heat treatment for drastically improved photocatalytic hydrogen with excellent photostability. Nano Energy 2017, 41, 1–9. [CrossRef]

24. Lu, N.; Wang, C.; Sun, B.; Gao, Z.; Su, Y. Fabrication of TiO2-doped single layer graphitic-C3N4 and its visible-light photocatalytic activity. Sep. Purif. Technol. 2017, 186, 226–232. [CrossRef]

25. Shi, H.; Long, S.; Hu, S.; Hou, J.; Ni, W.; Song, C.; Li, K.; Gurzadyan, G.G.; Guo, X. Interfacial charge transfer in 0D/2D defect-rich heterostructures for efficient solar-driven CO2 reduction. Appl. Catal. B 2019, 245, 760–769. [CrossRef]

26. Reli, M.; Huo, P.; Shior, M.; Ambrozová, N.; Troppová, I.; Matějová, L.; Lang, J.; Svoboda, L.; Kuśtworski, P.; Ritz, M.; et al. Novel TiO2-C3N4 photocatalysts for photocatalytic reduction of CO2 and for photocatalytic decomposition of N2O. J. Phys. Chem. A 2016, 120, 8564–8573. [CrossRef]

27. Zhang, L.; Xie, C.; Jiu, H.; Meng, Y.; Zhang, Q.; Gao, Y. Synthesized hollow TiO2@g-C3N4 composites for carbon dioxide reduction under visible light. Catal. Lett. 2018, 148, 2812–2821. [CrossRef]

28. Banitalebi Dehkordi, A.; Ziarati, A.; Ghasemi, J.B.; Badiei, A. Preparation of hierarchical g-C3N4@TiO2 hollow spheres for enhanced visible-light-induced catalytic CO2 reduction. Sol. Energy 2020, 205, 465–473. [CrossRef]
29. Zhou, S.; Liu, Y.; Li, J.; Wang, Y.; Jiang, G.; Zhao, Z.; Wang, D.; Duan, A.; Liu, J.; Wei, Y. Facile in situ synthesis of graphitic carbon nitride (g-C3N4)-TiO2 heterojunction as an efficient photocatalyst for the selective photoreduction of CO2 to CO. *Appl. Catal. B* 2014, 158–159, 20–29. [CrossRef]

30. Thanh Truc, N.T.; Giang Bach, L.; Thi Hanh, N.; Pham, T.-D.; Thi Phuong Le Chi, N.; Tran, D.T.; Nguyen, M.V.; Nguyen, V.N. The superior photocatalytic activity of Nb doped TiO2/g-C3N4 direct Z-scheme system for efficient conversion of CO2 into valuable fuels. *J. Colloid Interface Sci.* 2019, 540, 1–8. [CrossRef]

31. Li, H.; Gao, Y.; Wu, X.; Lee, P.-H.; Shih, K. Fabrication of heterostructured g-C3N4/Ag-TiO2 hybrid photocatalyst with enhanced performance in photocatalytic conversion of CO2 under simulated sunlight irradiation. *Appl. Surf. Sci.* 2017, 402, 198–207. [CrossRef]

32. Liu, C.; Raziq, F.; Li, Z.; Qu, Y.; Zada, A.; Jing, L. Synthesis of TiO2/g-C3N4 nanocomposites with phosphate–oxygen functional bridges for improved photocatalytic activity. *Chin. J. Catal.* 2017, 38, 1072–1078. [CrossRef]

33. Sun, R.; Jiang, X.; Zhang, M.; Ma, Y.; Jiang, X.; Liu, Z.; Wang, Y.; Yang, J.; Xie, M.; Han, W. Dual quantum dots decorated TiO2 nanorod arrays for efficient CO2 reduction. *J. Catal.* 2019, 378, 192–200. [CrossRef]

34. Wang, Y.; Li, B.; Zhang, C.; Cui, L.; Kang, S.; Li, Z.; Zhou, L. Ordered mesoporous CeO2-TiO2 composites: Highly efficient photocatalysts for the reduction of CO2 with H2O under simulated solar irradiation. *Appl. Catal. B* 2013, 130–131, 277–284. [CrossRef]

35. Abdullah, H.; Khan, M.R.; Pudukudy, M.; Yaakob, Z.; Ismail, N.A. CeO2-TiO2 as a visible light active catalyst for the photoreduction of CO2 to methanol. *J. Rare Earths* 2015, 33, 1155–1161. [CrossRef]

36. Jiao, J.; Wei, Y.; Zhao, Z.; Liu, J.; Li, J.; Duan, A.; Jiang, G. Photocatalysts of 3D Ordered Macroporous TiO2-Supported CeO2 nanolayers: Design, Preparation, and their catalytic performances for the reduction of CO2 with H2O under simulated solar irradiation. *Ind. Eng. Chem. Res.* 2014, 53, 17345–17354. [CrossRef]

37. Zhao, J.; Wang, Y.; Li, Y.; Yue, X.; Wang, C. Phase-dependent enhancement for CO2 photocatalytic reduction over CeO2/TiO2 catalysts. *Catal. Sci. Technol.* 2016, 6, 7967–7975. [CrossRef]

38. Wang, Y.; Zhao, J.; Wang, T.; Li, Y.; Li, X.; Yin, J.; Wang, C. CO2 photoreduction with H2O vapor on highly dispersed CeO2/TiO2 catalysts: Surface species and their reactivity. *J. Catal.* 2016, 337, 293–302. [CrossRef]

39. Qin, S.; Xin, F.; Liu, Y.; Yin, X.; Ma, W. Photocatalytic reduction of CO2 in methanol to methyl formate over CuO–TiO2 composite catalysts. *J. Colloid Interface Sci.* 2011, 356, 257–261. [CrossRef]

40. Méndez-Medrano, M.G.; Kowalska, E.; Lehoux, A.; Herissan, A.; Ohtani, B.; Bahena, D.; Briois, V.; Colbeau-Justin, C.; Rodríguez-López, J.L.; Remita, H. Surface modification of TiO2 with Ag nanoparticles and CuO nanoclusters for application in photocatalysis. *J. Phys. Chem. C* 2016, 120, 5143–5154. [CrossRef]

41. Zhao, Y.; Chen, J.; Cai, W.; Bu, Y.; Huang, Q.; Tao, T.; Lu, J. CuO-decorated dual-phase TiO2 microspheres with enhanced activity for photocatalytic CO2 reduction in liquid–solid regime. *Chem. Phys. Lett.* 2019, 725, 66–74. [CrossRef]

42. Li, H.; Li, C.; Han, L.; Li, C.; Zhang, S. Photoreduction of CO2 with H2O on CuO/TiO2 catalysts. *Energy Sources A Recovery Util. Environ. Eff.* 2016, 38, 420–426. [CrossRef]

43. Razali, M.H.; Yusoff, M. Highly efficient CuO loaded TiO2 nanotube photocatalyst for CO2 photoreduction. *Mater. Lett.* 2018, 221, 168–171. [CrossRef]

44. Park, H.; Ou, H.-H.; Kang, U.; Choi, J.; Hoffmann, M.R. Photocatalytic conversion of carbon dioxide to methane on TiO2/CdS in aqueous isopropanol solution. *Catal. Today* 2016, 266, 153–159. [CrossRef]

45. Low, J.; Dai, B.; Tong, T.; Jiang, C.; Yu, J. In situ irradiated X-ray photoelectron spectroscopy investigation on a direct Z-Scheme TiO2/CdS composite film photocatalyst. *Adv. Mater.* 2019, 31, 1802981. [CrossRef] [PubMed]

46. Song, G.; Xin, F.; Chen, J.; Yin, X. Photocatalytic reduction of CO2 in cyclohexanol on CdS–TiO2 heterostructured photocatalyst. *Appl. Catal. A* 2014, 473, 90–95. [CrossRef]

47. Ahmad Beigi, A.; Fatemi, S.; Salehi, Z. Synthesis of nanocomposite CdS/TiO2 and investigation of its photocatalytic activity for CO2 reduction to CO and CH4 under visible light irradiation. *J. CO2 Util.* 2014, 7, 23–29. [CrossRef]

48. Khalilzadeh, A.; Shariati, A. Photoreduction of CO2 over heterogeneous modified TiO2 nanoparticles under visible light irradiation: Synthesis, process and kinetic study. *Sol. Energy* 2018, 164, 251–261. [CrossRef]

49. Jia, P.-y.; Guo, R.-t.; Pan, W.-g.; Huang, C.-y.; Tang, J.-y.; Liu, X.-y.; Qin, H.; Xu, Q.-y. The MoS2/TiO2 heterojunction composites with enhanced activity for CO2 photocatalytic reduction under visible light irradiation. *Colloids Surf. A: Physicochem. Eng. Asp.* 2019, 570, 306–316. [CrossRef]

50. Xu, F.Y.; Zhu, B.C.; Cheng, B.; Yu, J.G.; Xu, J.S. 1D/2D TiO2/MoS2 hybrid nanostructures for enhanced photocatalytic CO2 reduction. *Adv. Opt. Mater.* 2018, 6, 1800911. [CrossRef]

51. Tu, W.; Li, Y.; Kua, L.; Zhou, Y.; Xu, Q.; Li, H.; Wang, X.; Xiao, M.; Zou, Z. Construction of unique two-dimensional MoS2–TiO2 hybrid nanojunctions: MoS2 as a promising cost-effective cocatalyst toward improved photocatalytic reduction of CO2 to methanol. *Nanoscale* 2017, 9, 9065–9070. [CrossRef]

52. Marci, G.; Garcia-Lopez, E.I.; Palmisano, L. Photocatalytic CO2 reduction in gas-solid regime in the presence of H2O by using GaP/TiO2 composite as photocatalyst under simulated solar light. *Catal. Commun.* 2014, 53, 38–41. [CrossRef]

53. Truong, Q.D.; Liu, J.-Y.; Chung, C.-C.; Ling, Y.-C. Photocatalytic reduction of CO2 on FeTiO3/TiO2 photocatalyst. *Catal. Commun.* 2012, 19, 85–89. [CrossRef]
54. Lin, J.; Hu, J.; Qiu, C.; Huang, H.; Chen, L.; Xie, Y.; Zhang, Z.; Lin, H.; Wang, X. In situ hydrothermal etching fabrication of CaTiO$_3$ on TiO$_2$ nanosheets with heterojunction effects to enhance CO$_2$ adsorption and photocatalytic reduction. *Catal. Sci. Technol.* **2019**, *9*, 336–346. [CrossRef]

55. Yin, S.; Han, J.; Zhou, T.; Xu, R. Recent progress in g-C$_3$N$_4$ based low cost photocatalytic system: Activity enhancement and emerging applications. *Catal. Sci. Technol.* **2015**, *5*, 5048–5061. [CrossRef]

56. Raizada, P.; Kumar, A.; Hasija, V.; Singh, P.; Thakur, V.K.; Khan, A.A.P. An overview of converting reductive photocatalyst into all solid-state and direct Z-scheme system for water splitting and CO$_2$ reduction. *J. Ind. Eng. Chem.* **2021**, *93*, 1–27. [CrossRef]

57. Journhabani, M.; Shariatinia, Z.; Badiei, A. Sulfur-doped mesoporous carbon nitride decorated with Cu particles for efficient photocatalytic degradation under visible-light irradiation. *J. Phys. Chem. C* **2017**, *121*, 19239–19253. [CrossRef]

58. Jiang, Z.; Wan, W.; Li, H.; Yuan, S.; Zhao, H.; Wong, P.K. A hierarchical Z-Scheme α-Fe$_2$O$_3$/g-C$_3$N$_4$ hybrid for enhanced photocatalytic CO$_2$ reduction. *Adv. Mater.* **2018**, *30*, 1706108. [CrossRef]

59. Ong, W.-J.; Tan, L.-L.; Ng, Y.H.; Yong, S.-T.; Chai, S.-P. Graphitic carbon nitride (g-C$_3$N$_4$)-based photocatalysts for artificial photosynthesis and environmental remediation: Are we a step closer to achieving sustainability? *Chem. Rev.* **2016**, *116*, 7159–7329. [CrossRef]

60. Zhao, Y.; Lin, Y.; Wang, G.; Jiang, Z.; Zhang, R.; Zhu, C. Electronic and optical performances of (Cu, N) codoped TiO$_2$/g-C$_3$N$_4$ heterostructure photocatalyst: A spin-polarized DFT + U study. *Sol. Energy* **2018**, *162*, 306–316. [CrossRef]

61. Chen, Y.; Huang, W.; He, D.; Situ, Y.; Huang, H. Construction of Heterostructured g-C$_3$N$_4$/Ag/TiO$_2$ Microspheres with Enhanced Photocatalysis Performance Under Visible-Light Irradiation. *ACS Appl. Mater. Interfaces* **2014**, *6*, 14405–14414. [CrossRef]

62. Jiang, G.; Cao, J.; Chen, M.; Zhang, X.; Dong, F. Photocatalytic NO oxidation on N-doped TiO$_2$/g-C$_3$N$_4$ heterojunction: Enhanced efficiency, mechanism and reaction pathway. *Appl. Surf. Sci.* **2018**, *458*, 75–85. [CrossRef]

63. Liu, R.; Bie, Y.; Qiao, Y.; Liu, T.; Song, Y. Design of g-C$_3$N$_4$/TiO$_2$ nanotubes heterojunction for enhanced organic pollutants degradation in waste water. *Mater. Lett.* **2019**, *251*, 126–130. [CrossRef]

64. Das, A.; Patra, M.; Kumar, P.M.; Bhagavathiachari, M.; Nair, R.G. Defect-induced visible-light-driven photocatalytic and photoelectrochemical performance of ZnO–CeO$_2$ nanoheterojunctions. *J. Alloys Compd.* **2021**, *858*, 157770. [CrossRef]

65. Islam, M.J.; Reddy, D.A.; Choi, J.; Kim, T.K. Surface oxygen vacancy assisted electron transfer and shuttling for enhanced photocatalytic activity of a Z-scheme CeO$_2$–AgI nanocomposite. *RSC Adv.* **2016**, *6*, 19341–19350. [CrossRef]

66. Basha, M.H.; Ramu, C.; Gopal, N.O.; Reddy, M.V.B. Structural and spectroscopic characterizations of boron doped TiO$_2$–CeO$_2$ nanocomposite synthesized by solution combustion technique for photocatalytic applications. *J. Mol. Struct.* **2021**, *1231*, 129892. [CrossRef]

67. Patil, P.; Nakate, U.T.; Nakate, Y.T.; Ambare, R.C. Acetaldehyde sensing properties using ultrafine CuO nanoparticles. *Mater. Sci. Semicond. Process.* **2019**, *101*, 76–81. [CrossRef]

68. Zhang, H.; Wang, K.; Wang, L.; Xie, H.; Yu, W. Mesoporous CuO with full spectrum absorption for photothermal conversion in direct absorption solar collectors. *Sol. Energy* **2020**, *201*, 628–637. [CrossRef]

69. Avila-Lopez, M.A.; Luevano-Hipolito, E.; Torres-Martinez, L.M. CuO coatings on glass fibers: A hybrid material for CO$_2$ adsorption and photocatalytic reduction to solar collectors. *J. Mater. Sci.—Mater. Electron.* **2021**, *32*, 11336–11337. [CrossRef]

70. Avila-Lopez, M.A.; Luevano-Hipolito, E.; Torres-Martinez, L.M. CO$_2$ adsorption and its visible-light-driven reduction using CuO synthesized by an eco-friendly sonochemical method. *J. Photochem. Photobiol. A—Chem.* **2019**, *382*, 10. [CrossRef]

71. Yan, Y.; Yu, Y.; Cao, C.; Huang, S.; Yang, Y.; Yang, X.; Cao, Y. Enhanced photocatalytic activity of TiO$_2$–Cu/C with regulation and matching of energy levels by carbon and copper for photo-reduction of CO$_2$ into CH$_4$. *CrystEngComm* **2016**, *18*, 2956–2964. [CrossRef]

72. Nogueira, A.E.; Oliveira, J.A.; da Silva, G.T.S.T.; Ribeiro, C. Insights into the role of CuO in the CO$_2$ photoreduction process. *Sci. Rep.* **2019**, *9*, 1516. [CrossRef]

73. Wang, Q.; Lian, J.; Ma, Q.; Zhang, S.; He, J.; Zhong, J.; Li, J.; Huang, H.; Su, B. Preparation of carbon spheres supported CdS photocatalyst for enhancement its photocatalytic H$_2$ evolution. *Catal. Today* **2017**, *281*, 662–668. [CrossRef]

74. Meng, H.L.; Cui, C.; Shen, H.L.; Liang, D.Y.; Xue, Y.Z.; Li, P.G.; Tang, W.H. Synthesis and photocatalytic activity of TiO$_2$@CdS and CdS@TiO$_2$ double-shelled hollow spheres. *J. Alloys Compd.* **2012**, *527*, 30–35. [CrossRef]

75. Li, X.; Chen, J.; Li, H.; Li, J.; Xu, Y.; Liu, Y.; Zhou, J. Photoreduction of CO$_2$ to methanol over Bi$_2$S$_3$/CdS photocatalyst under visible light irradiation. *J. Nat. Gas Chem.* **2011**, *20*, 413–417. [CrossRef]

76. Jang, J.S.; Park, H. Strategic Design of Heterojunction CdS Photocatalysts for Solar Hydrogen. In *Materials and Processes for Solar Fuel Production*; Viswanathan, B., Subramanian, V., Lee, J.S., Eds.; Springer: New York, NY, USA, 2014; pp. 1–22.

77. Tan, C.; Zhang, H. Two-dimensional transition metal dichalcogenide nanosheet-based composites. *Chem. Soc. Rev.* **2015**, *44*, 2713–2731. [CrossRef] [PubMed]

78. Xiang, Q.; Yu, J.; Jaroniec, M. Synergetic effect of MoS$_2$ and graphene as cocatalysts for enhanced photocatalytic H$_2$ production activity of TiO$_2$ nanoparticles. *J. Am. Chem. Soc.* **2012**, *134*, 6575–6578. [CrossRef] [PubMed]

79. Chen, B.; Meng, Y.; Sha, J.; Zhong, C.; Hu, W.; Zhao, N. Preparation of MoS$_2$/TiO$_2$ based nanocomposites for photocatalysis and rechargeable batteries: Progress, challenges, and perspective. *Nanoscale* **2018**, *10*, 34–68. [CrossRef] [PubMed]

80. Zhou, W.; Yin, Z.; Du, Y.; Huang, X.; Zeng, Z.; Fan, Z.; Liu, H.; Wang, J.; Zhang, H. Synthesis of few-layer MoS$_2$ nanosheet-coated TiO$_2$ nanobelt heterostructures for enhanced photocatalytic activities. *Small* **2013**, *9*, 140–147. [CrossRef]
81. Halmann, M. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature* 1978, 275, 115–116. [CrossRef]

82. Barton, E.E.; Rampulla, D.M.; Bocarsly, A.B. Selective Solar-Driven Reduction of CO₂ to Methanol Using a Catalyzed p-GaP Based Photoelectrochemical Cell. *J. Am. Chem. Soc.* 2008, 130, 6342–6344. [CrossRef]

83. Cañas-Martínez, D.M.; Cipagauta-Díaz, S.; Manrique, M.; Gómez, R.; Pedraza-Avellana, J.A. Photocatalytic hydrogen production using FeTiO₃ concentrates modified by high energy ball milling. *Top. Catal.* 2021, 64, 2–16. [CrossRef]

84. Cañas-Martínez, D.M.; Gauthier, G.H.; Pedraza-Avellana, J.A. Photo-oxidative and photo-reductive capabilities of ilmenite-rich black sand concentrates using methyl orange as a probe molecule. *Photochem. Photobiol. Sci.* 2019, 18, 912–919. [CrossRef] [PubMed]

85. Moradi, M.; Vasseghian, Y.; Khataee, A.; Harati, M.; Arfaeinia, H. Ultrasound-assisted synthesis of FeTiO₃/GO nanocomposite for photocatalytic degradation of phenol under visible light irradiation. *Sep. Purif. Technol.* 2021, 261, 118274. [CrossRef]

86. Xiao, W.; Lu, X.-g.; Zou, X.-l.; Wei, X.-m.; Ding, W.-z. Phase transitions, micro-morphology and its oxidation mechanism in oxidation of ilmenite (FeTiO₃) powder. *Trans. Nonferrous Met. Soc. China* 2013, 23, 2439–2445. [CrossRef]

87. Baysal, Z.; Kirchner, J.; Mehne, M.; Kureti, S. Study on the reduction of ilmenite-type FeTiO₃ by H₂. *Int. J. Hydrogen Energy* 2021, 46, 4447–4459. [CrossRef]

88. García-Muñoz, P.; Pliego, G.; Zazo, J.A.; Bahamonde, A.; Casas, J.A. Ilmenite (FeTiO₃) as low cost catalyst for advanced oxidation processes. *J. Environ. Chem. Eng.* 2016, 4, 542–548. [CrossRef]

89. Gao, B.; Yang, C.; Chen, J.; Ma, Y.; Xie, J.; Zhang, H.; Wei, L.; Li, Q.; Du, J.; Xu, Q. Ferromagnetic photocatalysts of FeTiO₃–Fe₂O₃ nanocomposites. *RSC Adv.* 2017, 7, 54994–54602. [CrossRef]

90. Zaraza-Morín, M.E.; Torres-Martínez, L.M.; Moctezuma, E.; Juárez-Ramírez, I.; Zermeño, B.B. Synthesis, characterization, and catalytic activity of FeTiO₃/TiO₂ for photodegradation of organic pollutants with visible light. *Res. Chem. Intermed.* 2016, 42, 1029–1043. [CrossRef]

91. Gao, B.; Kim, Y.J.; Chakraborty, A.K.; Lee, W.I. Efficient decomposition of organic compounds with FeTiO₃/TiO₂ heterojunction under visible light irradiation. *Appl. Catal. B* 2008, 83, 202–207. [CrossRef]

92. Passi, M.; Pal, B. A review on CaTiO₃ photocatalyst: Activity enhancement methods and photocatalytic applications. *Powder Technol.* 2021, 388, 274–304. [CrossRef]

93. Cesconeto, F.R.; Borlaf, M.; Nieto, M.I.; de Oliveira, A.P.N.; Moreno, R. Synthesis of CaTiO₃ and CaTiO₃/TiO₂ nanoparticulate compounds through Ca²⁺/TiO₂ colloidal sols: Structural and photocatalytic characterization. *Ceram. Int.* 2018, 44, 301–309. [CrossRef]

94. Zhu, Y.; Zhu, D.; Yan, Q.; Gao, G.; Xu, J.; Liu, Y.; Alahakoon, S.B.; Rahman, M.M.; Ajayan, P.M.; Egap, E.; et al. Metal Oxide Catalysts for the Synthesis of Covalent Organic Frameworks and One-Step Preparation of Covalent Organic Framework-Based Composites. *Chem. Mater.* 2021, 33, 6158–6165. [CrossRef]

95. Zhang, M.; Lu, M.; Lang, Z.-L.; Liu, J.; Liu, M.; Chang, J.-N.; Li, L.-Y.; Shang, L.-J.; Wang, M.; Li, S.-L.; et al. Semiconductor/Covalent-Organic-Framework Z-Scheme Heterojunctions for Artificial Photosynthesis. *Angew. Chem. Int. Ed.* 2020, 59, 6500–6506. [CrossRef] [PubMed]