Review

TiO$_2$ Based Nanostructures for Photocatalytic CO$_2$ Conversion to Valuable Chemicals

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Abstract: Photocatalytic conversion of CO$_2$ to useful products is an alluring approach for acquiring the two-fold benefits of normalizing excess atmospheric CO$_2$ levels and the production of solar chemicals/fuels. Therefore, photocatalytic materials are continuously being developed with enhanced performance in accordance with their respective domains. In recent years, nanostructured photocatalysts such as one dimensional (1-D), two dimensional (2-D) and three dimensional (3-D)/hierarchical have been a subject of great importance because of their explicit advantages over 0-D photocatalysts, including high surface areas, effective charge separation, directional charge transport, and light trapping/scattering effects. Furthermore, the strategy of doping (metals and non-metals), as well as coupling with a secondary material (noble metals, another semiconductor material, graphene, etc.), of nanostructured photocatalysts has resulted in an amplified photocatalytic performance. In the present review article, various titanium dioxide (TiO$_2$)-based nanostructured photocatalysts are briefly overviewed with respect to their application in photocatalytic CO$_2$ conversion to value-added chemicals. This review primarily focuses on the latest developments in TiO$_2$-based nanostructures, specifically 1-D (TiO$_2$ nanotubes, nanorods, nanowires, nanobelts etc.) and 2-D (TiO$_2$ nanosheets, nanolayers), and the reaction conditions and analysis of key parameters and their role in the up-grading and augmentation of photocatalytic performance. Moreover, TiO$_2$-based 3-D and/or hierarchical nanostructures for CO$_2$ conversions are also briefly scrutinized, as they exhibit excellent performance based on the special nanostructure framework, and can be an exemplary photocatalyst architecture demonstrating an admirable performance in the near future.

Keywords: TiO$_2$; 1-D nanostructures; 2-D nanostructures; hierarchical nanostructures; photocatalytic CO$_2$ conversion; reactions mechanism

1. Introduction

Enormous amounts of CO$_2$ emissions, mainly due to industrialization and burning of fossil fuels, are considered to be a primary source of global warming [1]. Hence, fossil fuel consumption for fulfilling energy demands has led to increased atmospheric CO$_2$ levels, along with depletion of respective resources. To deal with such a critical energy and environmental issue, developments in the field of renewable energy such as wind, hyde, biomass, nuclear and solar energy, are being carried out by global scientists and researchers. Among these, solar energy, in terms of its utilization in converting anthropogenic CO$_2$ into value-added chemicals on a photocatalyst surface in the presence of a reducing agent, is an alluring and auspicious research area to counter environmental pollution with the possibility of matching the renewable energy infrastructure [2]. The photocatalytic CO$_2$ conversion (PCC) to value-added chemicals like CO, CH$_4$, C$_2$H$_6$, C$_2$H$_5$OH, C$_2$H$_4$, CH$_3$OH, HCOOH,
etc., in general mimics the concept of natural photosynthesis and is considered a subordinate of the “Artificial Photosynthesis” research domain [2–5].

Since the invention of water photocatalysis by Fujishima and Honda in 1972 [6], TiO$_2$ photocatalysts have emerged as the premier and champion material with splendid properties including favorable surface area, non-toxicity, abundant availability, high stability, and cost effectiveness [7–9]. On the contrary, TiO$_2$ nanoparticles (0-D), with a disadvantage of only UV light absorption, also exhibit drawbacks of fast electron–hole recombination, slow charge transfer, limited light trapping and difficulty in reuse/recycling [10]. Despite the development of many alternative photocatalysts to TiO$_2$, TiO$_2$ still remains a distinguished and premier choice because of the specific above-mentioned attributes.

In the last few years, TiO$_2$-based nanostructured photocatalysts such as one-dimensional (1-D) [11–13], two-dimensional (2-D) [14–16], and three-dimensional (3-D) or hierarchical structures [17,18], have received massive attention in a variety of photocatalysis domains [19]. The distinct properties of large surface area, high aspect ratio, directional flow of photogenerated charges resulting in decreased charge recombination, light scattering, stability and improved reusability/recyclability—especially for 1-D arrays and hierarchical nanostructures—has made them valuable and worthwhile to employ in the photocatalysis research domain. Moreover, the synthesis strategies for the 1-D nanostructures are simple and facile; however, for 2-D and hierarchical nanostructured photocatalysts, fabrication is generally limited to following/adopting complicated procedures. Hence, due to their specific geometry configurations [20,21], 1-D (nanotubes, nanowires, nanorods, etc.) and 2-D (nanosheets, nanolayers, etc.) nanostructured photocatalysts provide an attractive and exemplary opportunity to overcome the limitations of 0-D nanoparticles restricting the performance of photocatalysts. Furthermore, 3-D and hierarchical nanostructures offer superb light trapping properties within specific nanostructures, resulting in a slow photon effect and improved photocatalytic performance. Despite the eminent benefits of TiO$_2$ nanostructured photocatalysts, to some extent, they possess limitations with respect to the ultra violet region (a small portion of terrestrial solar spectrum) in terms of light absorption due to their wider band gap (~3.0–3.2 eV). Therefore, to overcome such limitations, similar strategies are commonly adopted as for 0-D nanoparticles, including metal and non-metal doping [18,22–25], noble metal loading [16,26–29], graphene derivative coupling [30–33], and hetero-junctioning TiO$_2$ nanostructures through the coupling of low band gap materials [11,17,34–37].

In this review, the recent progress of TiO$_2$-based nanostructures employed for photocatalytic CO$_2$ conversion to useful/value added chemicals is briefly overviewed. The key parameters promoting the improvement of photocatalytic performance, as well as the potential benefits offered by important frameworks, i.e., 1-D, 2-D and hierarchical nanostructures, are discussed. The photocatalytic performance of the TiO$_2$-based nanostructured photocatalysts, along with their reaction conditions and procedures, is summarized. In short, this review is focused on the architectural engineering of TiO$_2$-based nanostructured photocatalysts, such that they offer excellent properties with enhanced photocatalytic performance.

2. Photocatalytic CO$_2$ Conversion: Fundamentals and Mechanism

As is well established, CO$_2$ in gaseous form is a thermodynamically stable molecule with a Gibbs free energy of $\Delta G^\circ = -394.4$ KJ·mole$^{-1}$ [38]. Thus, a suitable amount of energy is required to transform gaseous CO$_2$ into value-added products. Equation (1) (Gibbs free energy) and Equation (2) (overpotential) demonstrate that more negative potential than $E^\circ$ is needed to compensate the overpotential and make the $\Delta G^\circ$ negative enough for spontaneous conversion of CO$_2$ gaseous molecule to proceed.

$$\Delta G^\circ = nFE^\circ$$ (1)
where $\Delta G^\circ = $ Standard Gibbs free energy, $n=$ number of electrons involved in reaction, $F =$ Faraday constant (96485 Cmole$^{-1}$) and $E^\circ =$ standard potential of the respective reaction.

$$\eta = E - E^\circ$$

(2)

where $\eta =$ overpotential, $E =$ required potential and $E^\circ =$ standard potential.

Hence, the required overpotential can be supplied to the reaction mixture in one of several ways, including as thermal energy, electrical energy, chemical energy and solar energy. Among these sources, utilization of solar energy in the presence of a photocatalyst is considered to be one of the most sustainable and cost-effective approaches. Moreover, for the reason of high stability, it is quite difficult for a photocatalyst alone to reduce CO$_2$ into products; therefore, the reduction to CO$_2$ proceeds with the support of reducing agents such as H$_2$O, H$_2$, etc. [38,39], which can regenerate the photocatalyst by readily providing the electrons in order to fill the holes. In turn, protons are released, which react with the surface-adsorbed CO$_2$ and electrons to give the desired product: a relatively feasible and less energetic pathway. Such a process is commonly known as a “proton-assisted multi-electron photoreduction process”, and it is a commonly accepted mechanism for photocatalytic CO$_2$ conversion. Table 1 shows the redox potentials for various CO$_2$ reactions (at pH = 7.0 and E vs. NHE) with H$_2$O in vapor or liquid phase [40]. It can be noted that the selectivity of the product, another important parameter, can also be manipulated by aligning the conduction band and valence band edge of the photocatalyst with respect to the redox potentials of the reactions.

Table 1. Electrochemical redox potentials ($E^\circ$ vs. NHE, pH = 7.0) for CO$_2$ reduction into a variety of useful chemical products [4,40,41].

| No. | Reactions                                      | $E^\circ$ vs. NHE (V) |
|-----|------------------------------------------------|----------------------|
| 1   | CO$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ HCOOH  | -0.61 V              |
| 2   | CO$_2$ + 2H$^+$ + 2e$^-$ $\rightarrow$ CO + H$_2$O | -0.53 V              |
| 3   | CO$_2$ + 4H$^+$ + 4e$^-$ $\rightarrow$ HCHO + H$_2$O | -0.48 V              |
| 4   | CO$_2$ + 6H$^+$ + 6e$^-$ $\rightarrow$ CH$_3$OH + H$_2$O | -0.38 V              |
| 5   | CO$_2$ + 8H$^+$ + 8e$^-$ $\rightarrow$ CH$_4$ + 2H$_2$O | -0.24 V              |
| 6   | 2H$^+$ + 2e$^-$ $\rightarrow$ H$_2$            | -0.41 V              |

Water Oxidation Reactio |

| 7   | 2H$_2$O $\rightarrow$ O$_2$ + 4H$^+$ + 4e$^-$ | +0.81V               |

As mentioned above, the conversion or reduction of CO$_2$ is more feasible in the presence of reducing agents such as H$_2$O, H$_2$, etc. H$_2$O is commonly chosen as a reducing agent because it has benefits such as being inexpensive, less dangerous than gaseous reducing agents (H$_2$, H$_2$S, etc.), and it only requires simple handling. Thus, a reaction mixture of gaseous CO$_2$ and H$_2$O (vapors or liquid) or H$_2$ gas is commonly used for the photocatalytic conversion of CO$_2$ into the desired products. Upon light irradiation on the photocatalyst with a CO$_2$(g)/H$_2$O(g) or CO$_2$(g)/H$_2$(g) mixture, the photogenerated electrons are rapidly transferred to the adsorbed CO$_2$ on the photocatalyst surface, and the presence of protons (H$^+$, which are provided by the reducing agents) yields the desired products. The definitive reaction mechanism for photocatalytic CO$_2$ conversion is still in need of extensive research; however, based on the binding and bridging mode of CO$_2$ with a photocatalyst surface, two commonly accepted pathways reported in the literature [42–45] include (i) the carbene pathway, and (ii) the formaldehyde pathway.

The possible reactions reported in the literature for the carbene pathway are presented in Equations (3)–(11). It is expected that CO$_2$$^\bullet^-$ radicals are formed by the quick reaction of a single electron to the surface-adsorbed CO$_2$. These radicals can then react with protons/hydrogen radicals and electrons to form CO as an intermediate product, which is believed to be adsorbed onto the
photocatalyst surface, further reacting with electrons and protons in a multi-step process to produce CH$^*$ radical, carbene, methyl radical and finally methanol or methane as valuable products.

$$\text{CO}_2 + e^- \rightarrow \text{CO}_2^{*\cdot}$$  \hspace{1cm} (3)

$$\text{CO}_2^{*\cdot} + e^- + H^+ \rightarrow \text{CO} + \text{OH}^-$$  \hspace{1cm} (4)

$$\text{CO} + e^- \rightarrow \text{CO}^*$$  \hspace{1cm} (5)

$$\text{CO} + e^- + H^+ \rightarrow \text{C} + \text{OH}^-$$  \hspace{1cm} (6)

$$\text{C} + e^- + H^+ \rightarrow \text{CH}^*$$  \hspace{1cm} (7)

$$\text{CH}^* + e^- + H^+ \rightarrow \text{CH}_2$$  \hspace{1cm} (8)

$$\text{CH}_2 + e^- + H^+ \rightarrow \text{CH}_3^*$$  \hspace{1cm} (9)

$$\text{CH}_3^* + e^- + H^+ \rightarrow \text{CH}_4$$  \hspace{1cm} (10)

$$\text{CH}_3 + \text{OH}^- \rightarrow \text{CH}_3\text{OH}$$  \hspace{1cm} (11)

In the formaldehyde pathway, the monodentate configuration via binding of one oxygen atom to a metal (titanium) atom, or binding of materials surface oxygen atom to the carbon atom of CO$_2$, favors the formation of carboxyl radical (COOH). Carboxyl radical (COOH) can react with the protons/hydrogen radicals, forming formic acid, which proceeds through the multi-step process of electron accepting and dehydration reactions to produce formaldehyde, methanol and methane. The proposed reactions are presented in Equations (12)–(21).

$$\text{CO}_2 + e^- \rightarrow \text{CO}_2^{*\cdot}$$  \hspace{1cm} (12)

$$\text{CO}_2^{*\cdot} + H^+ \rightarrow \text{COOH}$$  \hspace{1cm} (13)

$$\text{COOH} + e^- + H^+ \rightarrow \text{HCOOH}$$  \hspace{1cm} (14)

$$\text{HCOOH} + e^- + H^+ \rightarrow \text{H}_2\text{OOC}^*$$  \hspace{1cm} (15)

$$\text{HC}^*\text{OOH} + e^- + H^+ \rightarrow \text{HCOH} + \text{H}_2\text{O}$$  \hspace{1cm} (16)

$$\text{HCOH} + e^- \rightarrow \text{H}_2\text{C}^\cdot\text{O}^-$$  \hspace{1cm} (17)

$$\text{H}_2\text{C}^*\text{O}^- + H^+ \rightarrow \text{H}_2\text{OHC}^*$$  \hspace{1cm} (18)

$$\text{H}_2\text{OHC}^* + e^- + H^+ \rightarrow \text{CH}_3\text{OH}$$  \hspace{1cm} (19)

$$\text{CH}_3\text{OH} + e^- + H^+ \rightarrow \text{CH}_3 + \text{H}_2\text{O}$$  \hspace{1cm} (20)

$$\text{CH}_3 + e^- + H^+ \rightarrow \text{CH}_4$$  \hspace{1cm} (21)

3. One-Dimensional (1-D) Nanostructured Photocatalysts

One dimensional (1-D) TiO$_2$ nanostructures, such as nanotubes, nanowires, and nanorods, have been a topic of great interest within the photocatalysis research domain, and they have a variety of applications. The key advantages offered by 1-D TiO$_2$ nanostructures include large surface areas, better charge transfer, improved adsorption capacity, and extended light absorption due to the light trapping and scattering effect [46]. Until now, a moderate amount of research has been done on the development of one-dimensional (1-D) TiO$_2$ photocatalysts with a key focus being on photocatalytic CO$_2$ conversion to hydrocarbon fuel/useful chemicals. Several strategies encompass heterojunction formation with other visible light active photocatalysts, doping, noble metals loading and graphene coupling for attaining the key aim of improved photocatalytic CO$_2$ conversion.
Xin et al. proposed CdS and Bi$_2$S$_3$ heterostructured TiO$_2$ nanotubes (CdS-TNT and Bi$_2$S$_3$-TNT) photocatalysts prepared by a simple two-step synthesis approach [47]. TNT was first prepared using an alkaline hydrothermal method, followed by deposition of CdS and Bi$_2$S$_3$ in a fixed concentration using a simple precipitation approach from their respective precursors. The prepared photocatalysts were tested under visible light irradiation for photocatalytic CO$_2$ conversion. The Bi$_2$S$_3$-TNT photocatalyst showed the maximum efficiency, yielding 224.6 $\mu$mol/L of CH$_3$OH after 5 h of irradiation, as compared to CdS-TNT (159.5 $\mu$mol/L) and pure TNT (102.59 $\mu$mol/L). The increased production rate is mainly attributed to the extended light absorption of heterostructured photocatalysts and their efficient photogenerated charge separation. The conduction band edges of both CdS and Bi$_2$S$_3$ lie well above the conduction band edge of TiO$_2$; therefore, upon light irradiation, the excited electron can easily flow to the conduction band of TiO$_2$ and might react with the adsorbed CO$_2$ species. A depiction of the band gap alignment and CO$_2$ conversion to CH$_3$OH is displayed in Figure 1a. Moreover, it was found that CdS and Bi$_2$S$_3$ deposition decreased the surface area and CO$_2$ adsorption, in comparison to pure TNT, but did not significantly affect the photocatalytic performance.

Another effective approach is coating the 1-D photocatalyst surface with a good CO$_2$ adsorbent, such as MgO-covered TiO$_2$ nanotube networks (TNN) [48]. The TNN were fabricated by subjecting Ti foil to alkaline hydrothermal reaction, which resulted in well-aligned TNN. The TNN was then dipped in magnesium salt solutions of various concentrations, followed by calcination in air to finally obtain MgO-covered TNN. It was observed that MgO coverage with optimum concentration displays higher CO and CH$_4$ yields when compared with bare TNN. Moreover, the deposition of platinum nanoparticles (Pt NPs) onto MgO-TNN greatly enhances the CO and CH$_4$ yield. The increased performance of MgO-TNN is attributed to the chemisorption of CO$_2$ molecules and their conversion to MgCO$_3$ species, which are more reactive with atomic H than linear CO$_2$ molecules in terms of giving the respective products. In addition, Pt NPs act as an electron trap for the efficient separation of photogenerated electron–hole pairs. The photocatalytic conversion of CO$_2$ into CO and CH$_4$ was displayed in Figure 1b.

Self-doping, such as the introduction of oxygen vacancies into the TiO$_2$, generally referred to as reduced TiO$_2$, is another attractive strategy for improving the photocatalytic performance. A recently published article reported the synthesis of black TiO$_2$ films comprised of unique porous grid-like structures using a simple and safe hydrothermal method [49]. The elemental analysis of the synthesized TiO$_2$ films displayed oxygen deficiency, indicating the presence of oxygen vacancies. When employed for photocatalytic CO$_2$ conversion, the black TiO$_2$ films exhibited improved CO and CH$_4$ yields as compared to pure TiO$_2$ film. The increased product yield was mainly attributed to the extended light absorption and the efficient charge separation resulting from the degree of defects caused by the

Figure 1. (a) Proposed mechanism of photocatalytic CO$_2$ conversion to CH$_3$OH employing CdS and Bi$_2$S$_3$ TNT photocatalysts (taken with permission from [47]). (b) Production yield of CO and CH$_4$ from Pt-MgO-covered TNN films (taken with permission from [48]).
oxygen vacancies. Another study proposed a novel heterostructure consisting of octahedral Cu$_2$O nanoparticle-loaded TiO$_2$ nanotube (TNT) arrays [50]. TNT arrays were prepared by a conventional electrochemical anodization method, while Cu$_2$O nanoparticles were deposited from Cu salt solution using an electrodeposition approach. The Cu$_2$O-TNT arrays were prepared with varied Cu$_2$O deposition times. It was observed that the Cu$_2$O-TNT arrays prepared with an electrodeposition time of 30 min showed the maximum CH$_4$ yield under visible light irradiation. However, under simulated solar light illumination, the Cu$_2$O-TNT arrays prepared with an electrodeposition time of 15 min exhibited the maximum CH$_4$ yield. The key factors to which the enhanced performance was attributed include: (i) TNT arrays provide better charge transportation and light absorption, (ii) optimum loading of Cu$_2$O nanoparticles leading to improved visible light performance, and (iii) well-aligned band edges of Cu$_2$O and TNT arrays leading to better charge separation. The proposed mechanism involved is displayed in Figure 2a.

Another investigation reported a simple strategy for synthesizing Cu-modified TiO$_2$ nanoflower films (TNF) for enhanced photocatalytic conversion of CO$_2$ into CH$_3$OH [51]. The synthesis methodology includes the growth of TNF on Ti foil using a hydrothermal method, followed by a microwave-assisted reduction process for Cu modification. The Cu-TNF with optimum loading of Cu (0.5 millimol concentration of Cu$^{2+}$) exhibited enhanced CH$_3$OH yield under UV-visible and UV light irradiation conditions, at a factor of 6 and 3.6 times higher than pure TNF. The increased CH$_3$OH yield was mainly attributed to good charge separation and local surface Plasmon resonance (LSPR), which were induced by Cu NPs providing hot electrons to contribute to the photocatalytic reactions. The possible mechanism involved in the photocatalytic conversion of CO$_2$ into CH$_3$OH is depicted in Figure 2b.

![Figure 2](image_url)

**Figure 2.** Schematic of the mechanism involved in the photocatalytic conversion of CO$_2$ into: (a) CH$_4$ employing Cu$_2$O NP-incorporating TNT (taken with permission from [50]), and (b) CH$_3$OH using Cu-modified TNF films (taken with permission from [51]).

Recently, Cheng et al. reported CdS and Cu$^{2+}$ ion deposition onto TiO$_2$ nanorod (TNR) array film, and investigated its performance under visible light irradiation [52]. The TNR film was synthesized using a hydrothermal approach, while Cu$^{2+}$ ions and CdS deposition were obtained using the cation adsorption and successive ionic layer reaction (SILAR) methods. Various samples were prepared by varying CdS deposition by SILAR cycles. The CdS-Cu$^{2+}$/TNR film prepared with 2 SILAR cycles showed the maximum ethanol yield under visible light irradiation, thus suggesting this to be the optimum sample. Moreover, the influence of the CO$_2$ flow rate and reaction temperature was also analyzed, and the optimal conditions for yielding maximum ethanol yield were found to be 4 mL/L and 80 °C.

Li et al. recently proposed a heterostructure of TiO$_2$ nanotubes with CoOx, fabricated with a specially designed synthesis strategy for grafting CoOx nanoparticles onto TNT and inducing defects through hydrogenation within the heterostructure by N$_2$/H$_2$ annealing [53]. The TNT employed in the investigation consisted of TiO$_2$ (B) and anatase (A) phases. Two different samples were prepared by
selecting the hydrogenation step before and after the deposition of CoOx NPs, denoted AB-H-CoOx and AB-CoOx-H, respectively. Moreover, a new concept of photothermal catalytic conversion (PTC) was employed for conversion of CO2 into useful products. It was observed that the TNT-CoOx sample prepared using the AB-H-CoOx sequence at a temperature of 393 K resulted in a greater CO and CH4 yield as compared to the other samples. The key parameters associated with this performance enhancement includes: (i) improved surface area, (ii) oxygen vacancies, which increase the CO2 adsorption on the surface sites, and (iii) upon light irradiation, the photogenerated electrons are trapped by oxygen defects, whereas the holes are rapidly transported by CoOx clusters, thereby resulting in efficient charge separation. The synthesis methodology and CO2 conversion rates are displayed in Figure 3.

Noble metal loading, such as with silver (Ag) and gold (Au) nanoparticles, is also an effective strategy for improving the photocatalytic performance of the material. A report presented a size-controlled study of 1-D TiO2 nanowires (TNW) loaded with Au NPs for photocatalytic conversion CO2 into value-added chemicals [54]. The TNW were synthesized using an alkaline hydrothermal approach followed by deposition of Au NPs using a well-established chemical reduction method. The loading with the Au NPs was optimized by varying the concentration of the respective salts. The 0.5% Au-TNW exhibited the highest yields of CO, CH4 and CH3OH (1237, 13 and 12.6 µmol/g h, respectively) under visible light irradiation as compared to pure TNW (9, 3 and 0 µmol/g h). Moreover, the effect of TNW size was also investigated, and it was found that TNW synthesized with a reaction time of 2 h offered the best performance due to its uniform and smooth surfaces and increased surface areas. Upon loading with Au NPs, the surface area was reduced a bit, but the performance was improved due to the synergetic effect of Au NPs, with smaller-sized NPs acting as electron extractors, while larger NPs injected hot electrons into the TNW conduction band as a result of the LSPR effect. The proposed mechanism for the Au-TNW in photocatalytic CO2 conversion is well displayed in Figure 4a. Similarly, TNW loaded with Ag nanoparticles [55] or a combination of both Au and Ag nanoparticles [56] exhibited an analogous performance attitude under UV and visible light irradiation. Another similar strategy involves the electrodeposition of Ag nanoparticles on the inner side of TiO2 nanotube (TNT) arrays [57]. The photocatalytic performance of Ag-TNT with respect to the conversion of CO2 was evaluated against pure TNT and Ag-TNT fabricated using a chemical bath deposition approach. The electrodeposited Ag NPs at a fixed voltage and time resulted in a uniform size distribution and good junctioning to the inner side of the TNT arrays. This heterostructure resulted in an enhanced CH4 yield with a small amount of CH3OH under light irradiation, as compared to
pure TNT arrays and those of Ag-TNT arrays fabricated using conventional chemical bath deposition. The performance enhancement of the prepared photocatalyst was attributed to the light scattering inside the TNT arrays, which led to a greater degree of light absorption by Ag NPs, thus intensifying the LSPR effect. A more intensified LSPR effect leads to the injection of hot electrons into the conduction band of TNT, and thus to efficient charge separation and reaction with the adsorbed CO₂ to yield CH₄ or CH₃OH. Su et al. proposed the deposition of palladium (Pd) nanoparticles onto TiO₂ nanowires (Pd-TNW) and evaluated photocatalytic performance by CO₂ conversion to CO and CH₄ [58]. TNW were synthesized using a hydrothermal approach, while Pd nanoparticles were deposited using a chemical reduction method. The Pd deposition was optimized by varying the Pd salt concentration, and it was found that 0.5% Pd-TNW exhibited the maximum CO and CH₄ yield, which was mainly attributed to the efficient electron separation of Pd from the TNW conduction band, resulting in rapid reaction with the adsorbed CO₂.

Another research work proposed replacing the noble metal loading with rGO sheets deposited onto TiO₂ nanotube arrays (TNT). Interestingly, using the designed synthesis strategy, the resulting photocatalyst consisted of TNT arrays covered with rGO sheets embedded TiO₂ nanoparticles [30]. When employed for photocatalytic CO₂ conversion, the resulting photocatalyst provided a CH₄ yield that was 4.4 times higher than that achieved with pure TNT arrays, which was mainly attributed to the improved charge separation and extended light absorption. This proposed scheme for photocatalytic CO₂ conversion is displayed in Figure 5a.

Similarly, various TiO₂ nanostructures, i.e., nanoparticles, nanotubes and nanosheets combined with graphene, have been synthesized and studied for the purposes of photocatalytic conversion of CO₂ into useful products [60]. Different synthesis procedures were adopted for each nanostructure; however, TiO₂ nanorods (TNR) were synthesized using a hydrothermal method and graphene compositing was also performed using the hydrothermal approach. The 1% graphene-TNR (GR-TNR) exhibited the highest yields of CO and CH₄, which was mainly attributed to the increased surface area and the better interaction of graphene and TNR leading to improved charge separation under UV and
visible light irradiation. The CO and CH$_4$ yields from the various GR-TNR investigated are shown in Figure 5b.

![Figure 5](image)

**Figure 5.** (a) Schematic view of photocatalytic conversion of CO$_2$ into CH$_4$ on rGO-TNT (taken with permission from [30]). (b) Production rate of CO and CH$_4$ from GR-TNR with varied concentrations of graphene (taken with permission from [60]).

Recently, Kar et al. proposed a novel strategy using flame-annealed TNT, resulting in mixed-phase (rutile and anatase) square-shaped nanotubes with defect-induced oxygen vacancies [61]. The TiO$_2$ nanotubes were fabricated using a conventional electrochemical anodization method, employing a water base and an ethylene glycol base as an electrolyte. The synthesized TNT were then flame-annealed using a propane torch at a temperature of 750 °C for about 2 min. The flame-annealed TNT (FANT) using a water-based electrolyte exhibited the highest CH$_4$ yield under simulated solar light and visible light irradiation of a 50 W LED lamp, and this was around 1.7 and 1.56 times higher than TNT. The improved performance of FANT (TNT prepared with a water-based electrolyte) was mainly attributed to the improved light absorption achieved by using a mixed phase of FANT, i.e., anatase and rutile, along with the well-aligned band edges of the rutile phase, which were 0.2 eV lower than in the anatase phase, resulting in efficient charge separation. The presence of Ti$^{3+}$ states was also observed, which might have been generated due to improper oxidation of TNT; hence, extending light absorption as a result of the presence of shallow defects. Moreover, the most important aspect of the square shape of FANT is its interaction with light, resulting in a higher density of electromagnetic hotspots, and thus also contributing to improved photocatalytic performance. The synthesis procedure for FANT and the proposed mechanism involved in photocatalytic CO$_2$ conversion are shown in Figure 6.

A summarized overview of the numerous TiO$_2$-based 1-D nanostructures reviewed, including product type and production rate, reaction conditions, and key process parameters influencing photocatalytic performance, is presented in Table 2.
Figure 6. (a) Schematic overview of the synthesis procedure for FANT, and (b) the proposed mechanism for photocatalytic conversion of CO$_2$ into CH$_4$ employing the FANT photocatalyst (taken with permission from [61]).

Table 2. Summary of various 1-D nanostructured photocatalysts, including reaction conditions, production of value-added chemicals by photocatalytic CO$_2$ conversion, and key parameters for performance improvement.

| 1-D Nanostructure                        | Light Source and Reactants                                                                 | Production Rate of Value-Added Chemicals                                                                 | Key Parameters for Improved Performance                                                                 | Ref.     |
|------------------------------------------|------------------------------------------------------------------------------------------|------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------|----------|
| CdS/TiO$_2$ nanotubes and Bi$_2$S$_3$/TiO$_2$ nanotubes | 500 W Xenon lamp CO$_2$ bubbled through a solution of Sodium hydroxide and sodium nitrite | After 5 h of irradiation CH$_3$OH: 102.5 µmol/L for TNT CH$_3$OH: 159.5 µmol/L for CdS/TNT CH$_3$OH and 224.6 µmol/L for Bi$_2$S$_3$/TNT | Improved surface area Light absorption enhancement Improved CO$_2$ adsorption Efficient electron–hole separation | [47]     |
| MgO amorphous layers on Pt loaded TiO$_2$ nanotubes networks | 300 W Hg lamp CO$_2$ bubbled through water for Pt loaded on 0.01 M MgO coated TiO$_2$ Nanotube Networks | CO: 10.4 ppm/h cm$^{-2}$, and CH$_4$: 100.2 ppm/h cm$^{-2}$ for Pt loaded on 0.01 M MgO coated TiO$_2$ Nanotube Networks | Improved CO$_2$ adsorption Enhanced electron–hole separation | [48]     |
| Black TiO$_2$ films with grid-like structures | 300 W Xenon lamp CO$_2$ bubbled through water | CO: 115 µmol/g h, and CH$_4$: 12 µmol/g h | Improved light absorption Improved charge separation due to extended charge lifetime | [49]     |
Table 2. Cont.

| 1-D Nanostructure | Light Source and Reagents | Production Rate of Value-Added Chemicals | Key Parameters for Improved Performance | Ref. |
|-------------------|---------------------------|----------------------------------------|----------------------------------------|------|
| Cu$_2$O nanoparticles modified TiO$_2$ nanotube arrays | 350 W Xenon lamp with and without UV cutoff filter, CO$_2$ bubbled through water | After 4 h of irradiation using simulated solar light CH$_3$: 400 ppm/g for sample with 15 min of Cu$_2$O electrodeposition After 4 h of visible light irradiation CH$_4$: 8 ppm/g for sample with 30 min of Cu$_2$O electrodeposition | Visible light absorption by Cu$_2$O TNT providing a pathway for efficient electron-hole charge separation | [50] |
| Cu deposited on TiO$_2$ nanoflowers films | 500 W Xenon lamp with UV cutoff filter, CO$_2$ bubbled through water | CH$_3$OH: 1.8 µmol/cm$^2$ h under UV and Visible light irradiation For 0.5 Cu/TiO$_2$ film | LSPR effect due to Cu nanoparticles and efficient charge transfer property | [51] |
| Au nanoparticles deposited on TiO$_2$ nanowires | HID 35 W Car lamp, CO$_2$ and H$_2$ gaseous mixture | CO: 127 µmol/g h, CH$_4$: 13 µmol/g h, and CH$_3$OH: 12.65 µmol/g h For 0.5 Au TiO$_2$ NW | Efficient photogenerated charge extraction Improved Surface area | [54] |
| ZnFe$_2$O$_4$ nanoparticles on TiO$_2$ nanobelts | 250 W high pressure Hg lamp, CO$_2$ and cyclohexanol | After 8 h of UV illumination Cyclohexanone (CH): 170.2 µmol/g and Cyclohexyl formate (CF): 178.1 µmol/g With sample containing 9.78 wt. % loading of ZnFe$_2$O$_4$ | Improved Charge separation by a Z-scheme mechanism Enhanced Surface area | [59] |
| TNT arrays covered with rGO TiO$_2$ nanoparticles | 100 W Xenon solar simulator, CO$_2$ and Water vapors | CH$_4$: 5.67 ppm/cm$^2$ h | Efficient Charge separation Improved Surface area Light absorption enhancement | [30] |
| Ag NP's TiO$_2$ nanowires | 35 W HID car lamp as visible light source, 200 W Hg Reflector lamp as a UV light source, CO$_2$ and H$_2$ at feed ratio of 1.0, temperature 100 °C and Pressure 1 atm. | CO: 983 µmol/g h CH$_4$: 9.73 µmol/g h CH$_3$OH: 13 µmol/g h From 3% Ag deposited TiO$_2$ NWs | Moderate surface areas LSPR effects and efficient charge separation | [55] |
| Au-Ag NP's TiO$_2$ nanowires | 35 W HID car lamp as visible light source, 200 W Hg Reflector lamp as a UV light source, CO$_2$ and H$_2$ at feed ratio of 1.0, temperature 100 °C and Pressure 1 atm. | CO: 1813 µmol/g h CH$_4$: 35 µmol/g h C$_2$H$_4$: 0.95 µmol/g h C$_2$H$_6$: 2.52 µmol/g h C$_3$H$_8$: 3.94 µmol/g h C$_4$H$_{10}$: 3.82 µmol/g h CH$_3$OH: 18.76 µmol/g h From 2% Ag-0.5% Au deposited TiO$_2$ NWs | Improved surface area LSPR effects and efficient charge separation | [56] |
| Ag loaded TiO$_2$ nanotube arrays (TNT) | 300 W Xenon arc lamp with a 400 nm cutoff filter, CO$_2$ and water vapors | CH$_4$: 48 mmol/h m$^2$ Using the sample with electrodeposited Ag NPs at 3 V and 1 min | Schottkey Junction formation and SPR effect leading to injection of hot electrons to TiO$_2$ CB | [57] |
| CdS QDs-Cu$_2$O-TiO$_2$ nanorods (NR) | 300 W solar simulated Xenon lamp, CO$_2$ and water vapors mixture, Temperature of 80 °C | C$_2$H$_5$OH: 109.12 µmol/g h Using sample with 2 SILAR cycles CdS QDs-0.02 M Cu$_2$O ion onto TiO$_2$ NRs | Improved surface area Extended light absorption of the photocatalysts | [52] |
| Graphene QDs deposited TiO$_2$ nanotube arrays (TNT) | 100 W Xenon Solar simulator, CO$_2$ and water vapors | CH$_4$: 1.98 ppm/h cm$^2$ Employing G-TNT 3 sample prepared with 3 sec electrophoretic deposition time of GQDs | Enhanced light absorption with efficient extraction of photogenerated electron–hole pairs | [31] |
was observed that when the amount of urea was lower than a certain limit, it acted as an N-doping source.

The proposed mechanism for the g-C$_3$N$_4$ nanosheets nanostructure (TNS-CNN) is shown in Figure 7b. Noticeably, it was observed that when the amount urea was lower than a certain limit, it acted as a N-doping source of TiO$_2$. However, upon increasing the urea concentration, a composite of g-C$_3$N$_4$ and N-TiO$_2$ was obtained. Such variation resulted in the selectivity of the product, yielding CH$_4$ for N-TiO$_2$ and CO for the g-C$_3$N$_4$/N-TiO$_2$ composite. The product selectivity is attributed to the alignment of the band edges with respect to the redox potentials of prospective products. The g-C$_3$N$_4$/N-TiO$_2$ with 70:30 mole ratio resulted in the maximum yield of CO only, and no CH$_4$. However, the sample prepared with 50:50 mole ratio exhibited production of both CO and CH$_4$. The increased photocatalytic yield of CO and CH$_4$ was mainly attributed to the visible light absorption, moderate surface areas, enhanced interfacial charge transfer, and the alignment of band edges in accordance with product redox potentials. The transmission electron microscopy (TEM) image of the layered structure of N-TiO$_2$ nanoparticles loaded onto g-C$_3$N$_4$ nanosheets is displayed in Figure 7a. The proposed mechanism for the g-C$_3$N$_4$/N-TiO$_2$ is shown in Figure 7b.

Similarly, another recently published report proposed an in situ pyrolysis approach for the synthesis of a TiO$_2$ nanosheets-g-C$_3$N$_4$ nanosheets nanostructure (TNS-CNN) [63]. Figure 7c shows the TEM image for the TNS-CNN, clearly displaying the fractions of TNS on the CNN. TNS-CNN has been employed for photocatalytic CO$_2$ conversion using both H$_2$O and H$_2$ as reducing agents. It was observed that TNS-CNN provided a CO yield almost 12 times higher than pristine TNS and}

| 1-D Nanostructure                  | Light Source and Reactants | Production Rate of Value-Added Chemicals | Key Parameters for Improved Performance | Ref.  |
|------------------------------------|----------------------------|----------------------------------------|----------------------------------------|-------|
| Graphene TiO$_2$ nanostructures including nanoparticles, nanotubes and nanosheets | 300 W Xenon lamp, CO$_2$ and water vapors | CO: 7.58 µmol/g·h, CH$_4$: 12.3 µmol/g·h, By 1% graphene TiO$_2$ nanotubes | Increased surface area, Increased interaction between the photogenerated electrons, Improved CO$_2$ adsorption | [60]  |
| Flame annealed TiO$_2$ nanotubes (FANT) | 100 W Xenon solar simulator, Also 50 W LED lamps, employed as a visible light source, CO$_2$ and water vapors | CH$_4$: 156 µmol/g·h, From FANT-aq, synthesized using water as an electrolyte medium | Visible light activity due to defect mediated performance enhancement, Higher density of electromagnetic hotspots for visible light and stronger absorption of UV light | [61]  |
| Pd-TiO$_2$ nanowires (NW) | 400 W Hg Lamp, CO$_2$ and Water vapors | After 8 h of irradiation: CO: 50.4 µmol/g, CH$_4$: 26.7 µmol/g, Using 0.5% Pd-TiO$_2$ NW | Pd NPs acts as an electron transfer mediator leading to improved charge transfer | [58]  |
| TiO$_2$ nanotubes (NT) coated with CoO$_x$ nanoclusters | 150 W UV lamp with temperature increased to 393 K, CO$_2$ and water vapors | After 8 h of irradiation: CO: 16.403 µmol/g, CH$_4$: 10.051 µmol/g·s | Improved surface areas, Efficient photogenerated electrons-holes separation, Oxygen vacancies, improved CO$_2$ adsorption | [53]  |
37% higher than TiO$_2$-P25 (with H$_2$ as a reducing agent). When H$_2$O was employed as a reducing agent, the CO yield decreased to one third that obtained when using H$_2$ as a reducing agent. This is mainly attributed to the competition for H$_2$ produced as a side reaction of water splitting, along with its reducing capability. The overall performance might be attributed to the increased surface area, the enhanced interfacial charge transfer between the nanosheets, the effectiveness of H$_2$ as a reducing agent, and the visible light absorption of the CNN. A schematic representation of the CO$_2$ conversion mechanism is shown in Figure 7d.

![Figure 7](image_url)

Figure 7. (a) TEM image showing the loading of N-TiO$_2$ nanoparticles onto g-C$_3$N$_4$ nanosheets, and (b) proposed scheme involved in photocatalytic CO$_2$ conversion (taken with permission from [62]). (c) TEM image showing the 2-D nanostructure of TiO$_2$ nanosheets coupled with g-C$_3$N$_4$ nanosheets, and (d) schematic view of the interfacial charge transfer within TNS-CNN with the proposed photocatalytic CO$_2$ conversion mechanism (taken with permission from [63]).

Recently, Shi et al. reported defect-rich TiO$_2$ quantum dots (QDs) embedded within g-C$_3$N$_4$ nanosheets (TiO$_2$-$x$/g-C$_3$N$_4$) for efficient photocatalytic conversion of CO$_2$ into CO under solar light irradiation [64]. The fabricated TiO$_2$-$x$/g-C$_3$N$_4$ nanostructure exhibited a superior photocatalytic performance with a CO yield 5 times higher than that of pristine g-C$_3$N$_4$. The TiO$_2$-$x$/g-C$_3$N$_4$ was synthesized by a novel and facile strategy of in situ pyrolysis of melamine with MIL-125-NH$_2$ (Ti). Various samples were prepared with varying the mass ratios. The improved photocatalytic performance was mainly attributed to the improved light absorption, which extended towards the red region, the enhanced CO$_2$ adsorption due to the defective TiO$_2$ QDs, the efficient charge separation, as confirmed by transient photocurrent and photoluminescence spectroscopy, and the large surface area due to the nanostructured architecture of the material. Figure 8a displays the SEM image of a representative sample of sheet-type g-C$_3$N$_4$ embedded with 0-D TiO$_2$-$x$ nanoparticles. The proposed photocatalytic mechanism is depicted in Figure 8b, which provides a clear demonstration of the alignment of the band edges to the redox potentials. It can be seen that upon light irradiation TiO$_2$-$x$/g-C$_3$N$_4$ generates electron–hole pairs, and the electrons from the conduction band of g-C$_3$N$_4$ flow towards the conduction band of TiO$_2$-$x$, where in the presence of Co(bpy)$_3^{2+}$, the co-catalyst reacts sharply with the adsorbed
CO₂ to provide CO. In contrast, the holes within the TiO₂−x and g-C₃N₄ are regenerated by the Triethanolamine (TEOA) hole scavenger.

![Image](image1.png)

Figure 8. (a) SEM image of a representative TiO₂−x/g-C₃N₄ sample displaying sheet-type g-C₃N₄ embedded with TiO₂−x nanoparticles, and (b) schematic of the electronic structure of TiO₂−x/g-C₃N₄ with the proposed mechanism of photocatalytic CO₂ conversion (taken with permission from [64]).

Ultrathin TiO₂ nanosheets, prepared from a TiO₂-Octylamine lamella structure, resulted in an efficient photocatalyst for CO₂ conversion [65]. The extravagant increase in the surface area of the TiO₂ nanosheets led to greater light absorption and an increased number of CO₂ adsorption active sites. It was observed that, in order to obtain ultrathin nanosheets, decreasing the bulk thickness towards atomic-scale thickness might provide the surface atoms with efficient surface active sites for photocatalytic CO₂ conversion. Moreover, the fluorescence lifetime of the photogenerated charge within the ultrathin TiO₂ nanosheets was observed to be higher when compared to their bulk counterparts; therefore, suggesting that the ultrathin nanosheets provide an efficient charge separation pathway along its 2-D channels. As a result of the contributions of such parameters, the formate formation from ultrathin TiO₂ nanosheets was around 450 times higher than that of bulk TiO₂. Figure 9a shows a SEM image of ultrathin TiO₂ nanosheets, while Figure 9b displays a schematic view of the CO₂ conversion mechanism.

Recently, Liu et al. reported the fabrication of TiO₂ ultrathin nanosheets (TiO₂-U) using a simple hydrothermal approach followed by Pt nanoparticle deposition using a photochemical deposition method [66]. The Pt-TiO₂-U, when employed for photocatalytic CO₂ conversion, resulted in increased CO (54.2 μmol/g h) and CH₄ (66.4 μmol/g h) yields when compared to the pristine and reference samples. It was observed that TiO₂-U exhibited visible light absorption, indicating the presence of oxygen vacancies, which were confirmed by X-ray photoelectron spectroscopy (XPS) and electron paramagnetic resonance (EPR) analysis. The appearance of such self-defects (oxygen vacancies or Ti³⁺ states) was attributed to the narrowing of the thickness, leading to the formation of uncoordinated surface sites, as shown in Figure 9c. Such defects with respect to Ti³⁺ promote the adsorption of CO₂ and the uniform deposition of Pt nanoparticles. The improved photocatalytic performance was mainly attributed to the increased surface area, extended light absorption and CO₂ adsorption sites, and enhanced electron–hole separation by Pt nanoparticles. A schematic view of the photocatalytic mechanism is shown in Figure 9d.
Surface modification of the photocatalyst is another effective approach, leading to improved surface characteristics for photocatalytic CO2 conversion \[67\]. One research work reported that the acidification of TiO2 nanosheets using sulfuric acid led to enhanced CH4 yield after 4 h of light irradiation. Acidification did not affect the sheet structure or the exposed facet of the material. However, the surface area decreased a bit due to acid molecules plugging the pores. Moreover, the acid treatment extended the light absorption of the material towards the red region; this was mainly ascribed to the generation of oxygen vacancies during the process. Such vacancy formation also enhanced the electron–hole separation under light irradiation, leading to improved photocatalytic performance.

Lamellar structures also promote the photocatalytic activity by adsorbing photoactive species within the layers. Such layered structures with improved surface area and loading with visible active materials can lead to efficient photocatalysts, as proposed by Junior et al. \[68\]. The authors reported a TiO2 pillared K2Ti4O9 2-D structure loaded with visible light-active Cu2O nanoparticles. The introduction of TiO2 pillars into layered K2Ti4O9 drastically increased the surface area, which was further increased after loading with Cu2O nanoparticles. Also, the loading with Cu2O nanoparticles shifted the light absorption toward the red region, along with efficient charge separation at the interface of TiO2, K2Ti4O9 and Cu2O. All the mentioned parameters improved the photocatalytic yield of CH3OH from moist CO2, with a yield 2 times as high as that obtained from the pristine sample. The schematic depiction of the mechanism involved is presented in Figure 10a.
Another interesting and excellent approach to developing 2-D nanostructures is the growth of photocatalytic material onto a 2-D conductive substrate. Recently, Low et al. reported a simple approach for synthesizing TiO\(_2\) nanoparticles coated onto a conductive Ti\(_3\)C\(_2\) MXenes (TT) [69]. The TiO\(_2\) nanoparticles appeared as the Ti\(_3\)C\(_2\) MXenes were calcined at different temperatures and tested for photocatalytic CO\(_2\) conversion. When employed, the photocatalytic yield of CH\(_4\) was found to be 3.7 times higher than that of commercial TiO\(_2\)-P25. Figure 10b displays the SEM image of the TT sample calcined at 550 °C, which was the optimum sample. It can be seen that, upon calcination, TiO\(_2\) nanoparticles appear on the surface and edges of the layered Ti\(_3\)C\(_2\) MXenes, resulting in a rougher surface and an improved surface area. Upon testing for photocatalytic CO\(_2\) conversion, the optimum sample, TT550, yielded the maximum CH\(_4\) production, with minor production of CH\(_3\)OH and C\(_2\)H\(_5\)OH. Increasing the temperature beyond this point, the photocatalytic performance decreased due to the lower content of conductive Ti\(_3\)C\(_2\) MXenes. Therefore, it can be concluded that the presence of Ti\(_3\)C\(_2\) MXenes as a conductive pathway offered efficient separation of electron–hole pairs, leading to improved performance. In addition, the improved surface area contributed significantly by providing more reactive sites for CO\(_2\) adsorption and conversion. The proposed scheme for photocatalytic CO\(_2\) conversion is displayed in Figure 10c.

Another study reported Bi\(_2\)WO\(_6\)-TiO\(_2\) binanosheets (BT) as a 2-D nanostructure for photocatalytic conversion of CO\(_2\) into CO and CH\(_4\) [70]. The study mainly aimed to provide an enlightened view regarding carbonaceous intermediates or surface species in the generation of value-added chemicals. However, when tested under CO\(_2\) gas, it was observed that the BT sample exhibited enhanced yields of CO and CH\(_4\) when compared to the pristine samples. The key causes were ascribed to the improved interfacial charge transfer and the Z-scheme mechanism, which were deemed to be solely responsible for the enhanced photocatalytic performance. Table 3 provides a summarized overview of the numerous TiO\(_2\)-based 2-D nanostructures employed for photocatalytic conversion of CO\(_2\) into various products, with their production rate, reaction conditions and the key process parameters promoting photocatalytic performance.
Table 3. Summary of various 2-D nanostructured photocatalysts with reaction conditions, value-added chemicals produced as a result of photocatalytic CO₂ conversion, and key parameters for improved performance.

| 2-D Nanostructure | Light Source and Reactants | Production Rate of Value-Added Chemicals | Key Parameters for Improved Performance | Ref. |
|-------------------|--------------------------|------------------------------------------|----------------------------------------|------|
| g-C₃N₄/N-TiO₂ nanosheets | 300 W Xe arc lamp, CO₂ bubbled through Deionized water | After 12 h of irradiation: CO: 14.73 μmole/g, employing CT7 sample; CH₄: 5.71 μmole/g, employing sample CT5 | Moderate surface area; Efficient light absorption; Efficient charge separation at the heterojunction; Product selectivity due to band regulation | [62] |
| TiO₂ nanosheets modified with sulfuric acid | 500 W Xe Arc lamp, CO₂ and water vapors | After 4 h of irradiation: CH₄: 7.63 μmole/g | Acidification facilitates oxidation of water by Ti-OH; Ti³⁺ active sites i.e., oxygen vacancies; enhanced adsorption of CO₂; Efficient charge separation | [67] |
| Ultrathin TiO₂ nanosheets | 300 W Hg Lamp, CO₂ bubbled through Solution of photocatalyst powder in water | Formate formation 1.9 μmole/g h; 450 times higher than counterpart; 9 time higher than commercially available anatase TiO₂; Surface area increased; Promoted life time of electron; Efficient charge separation across the 2-D path | [65] |
| Cu₂O nanoparticles loaded on TiO₂ pillared K₂Ti₄O₇ layers | Polychromatic light AM 1.5 from solar simulator, CO₂ and water vapors | After 5 h of irradiation: CH₃OH: 2.93 μmole/g, 2 times more as compared to pristine sample | Increased surface area; Visible light absorption; Efficient charge separation | [68] |
| Cu modified g-C₃N₄ sheets with TiO₂ nanoparticles | 254 nm UV Lamp as a UV light source, 500 W Xe arc lamp as a visible light source, CO₂ bubbled through the water solution containing photocatalyst sample | After 8 h of irradiation under UV light: CH₃OH: 2574 μmole/g, HCOOH: 5069 μmole/g; Under Visible light: CH₃OH: 614 μmole/g, HCOOH: 6709 μmole/g; Optimum sample: 3 wt.% Cu and 30/70 ratio of g-C₃N₄ and TiO₂; Extended light absorption and efficient charge separation by copper doping; Band edges alignment reflects the selectivity for CH₃OH and HCOOH | [71] |
| TiO₂ nanoparticles on Ti₃C₂ nanesheets | UV LED 3 W 365 nm, CO₂ and water vapor generated in situ by reaction of NaHCO₃ and HCl | CH₃OH: 0.22 μmole/h for 50 mg sample with small amounts of CH₃OH and C₂H₅OH | Improved surface area; Nanosheets providing active sites; Efficient electron hole separation | [69] |
| Pt nanoparticles loaded ultrathin TiO₂ nanosheets | 300 W Xenon lamp, CO₂ and Water vapors | CH₄: 66.4 μmole/h, g CO: 54.2 μmole/h | 26 times higher surface area; Efficient electron hole separation; Improved CO₂ adsorption due to defective surface | [66] |
| 2-D g-C₃N₄ with 0-D TiO₂₋ₓ nanoparticles | 300 W Xenon lamp, CO₂ bubbled through solution containing 5 mg photocatalyst dispersed in 5 mL of solution of MeCN/TEOA with cocatalyst of Co(bpy)₃²⁺ | After 5 h of irradiation: CO: 388.9 μmole/g, 5 times higher than pristine g-C₃N₄; Promoted charge transfer due to electron channel formed between g-C₃N₄ and TiO₂ | [64] |
5. Hierarchical Nanostructures: A Dynamic and Potent Approach

In recent years, hierarchical nanostructures have received wider attention for the purpose of heterogeneous photocatalysis, as they possess admirable and exemplary properties at the micro/nanometer scale. Since the invention of 3-D/hierarchical nanostructures, intensive research has been carried out with the aim of developing competent and efficient hierarchical nanostructures for a variety of photocatalysis applications [21,72]. Based on nano-sized building blocks such as nanotubes, nanorods, nanosheets, etc., these nanostructures possess superb properties, including porous and interconnected networks, high surface areas, multi-dimensional domains for efficient charge transfer, improved light harvesting, and increased reactant adsorption, which together lead to enhanced photocatalytic performance. Therefore, these captivating aspects of hierarchical nanostructures provide a potentially dynamic opportunity to pursue the development of nanostructured photocatalysts to be employed for the photocatalytic conversion of CO\textsubscript{2} into useful chemicals/fuels.

Recently, Wang et al. proposed a 3-D hierarchical TiO\textsubscript{2} microsphere (MS) with tunable pore and chamber size to facilitate the diffusion of the gas and its subsequent photocatalytic conversion under simulated solar light irradiation [73]. Three different types of TiO\textsubscript{2} microspheres were prepared, i.e., solid MS, yolk/shell MS and hollow MS. Photocatalytic activities were tested under both UV and simulated solar light irradiation. It was observed that under UV light, solid MS exhibited the maximum CO yield (17.7 \mu\text{mol/g h}), which was 1.2 and 1.6 times higher than that obtained with yolk/shell MS and hollow MS, respectively. This increase in yield was attributed to the intense light absorption of solid MS. However, under simulated solar light irradiation, hollow MS showed the maximum CO yield (34 \mu\text{mol/g, after 3 h of irradiation}), which was 1.6 and 1.4 times higher than the yields obtained with solid and yolk/shell MS, respectively. The increased photocatalytic performance under simulated solar light was ascribed to the increased pore size of the hollow MS, leading to rapid diffusion of CO\textsubscript{2} molecules towards active sites, which is a result of its unique hierarchical nanostructure. Figure 11 shows SEM images of all of the MS samples and their CO production rate under simulated solar light irradiation.

Figure 11. SEM images of (a) solid MS, (b) yolk/shell MS, and (c) hollow MS. (d) CO production rate for various samples via photocatalytic CO\textsubscript{2} conversion (taken with permission from [73]).
Similarly, a recent report presented the replication of Camella tree leaves for synthesis of a unique porous TiO$_2$ architecture with enhanced photocatalytic conversion of CO$_2$ into CH$_4$ and CO [74]. The TiO$_2$ artificial leaves (AL) were synthesized using a bio-template approach. The unique architecture of the AL consists of interconnected nanosheets, leading to improved porosity and a surface area greater than that of TiO$_2$-P25. The photocatalytic CO$_2$ conversion was tested under both UV and visible light irradiation. Under UV light irradiation, the AL yielded mostly CH$_4$, whereas reference nonporous P25 yielded CO. This difference was attributed to the increased residence time and contact between reactant and catalyst within the porous network of the AL. Similar results were obtained when irradiated with visible green light; however, upon loading the Ru$_2$O nanoparticles, the CO and CH$_4$ yields with AL were drastically increased, which can be attributed to the efficient charge separation at the metal–semiconductor junction. Thus, the factors of porous networks with surface defects, increased surface area and efficient charge separation lead to improved photocatalytic performance in the AL hierarchical nanostructure. Figure 12 shows an image of the porous hierarchical TiO$_2$ AL obtained using the bio-template approach, and the rate of photocatalytic conversion of CO$_2$ into CH$_4$ and CO under UV and visible light sources.

![Image of camellia leaf, SEM image of artificial leaf displaying a porous structure, and the production rate of CO and CH$_4$ via the photocatalytic conversion of CO$_2$ and water vapors (taken with permission from [74]).](image)

Another work presented the fabrication of a 3-D Z-scheme nanostructured photocatalyst consisting of ZnIn$_2$S$_4$ nanosheets assembled onto TiO$_2$ nanobelts [75]. This hierarchical nanostructure, with an optimum ratio of ZnIn$_2$S$_4$ (0.33:1 mole ratio), exhibited an enhanced CH$_4$ yield (1.135 µmol/g h) from the photocatalytic conversion of CO$_2$ and water vapors under UV-visible light irradiation, which is around 39 times higher than the yield obtained from bare ZnIn$_2$S$_4$ nanosheets. The increased CH$_4$ yield was attributed to the improved surface area, light absorption and effective charge separation due to the Z-scheme mechanism. Figure 13a,b shows the CH$_4$ production rate from photocatalytic CO$_2$ conversion.
Kim et al. developed a unique architecture composed of Cu$_2$O dendrites covered with S-TiO$_2$ micro-blocks and CuO nanowires, resulting in a p-n-p heterojunction formation [76]. When employed in photocatalytic CO$_2$ conversion, this nanostructure yielded a high CH$_4$ production rate, at 2.31 µmole/m$^2$ h, which is ten times higher than with TiO$_2$ nanotubes. The increased CH$_4$ yield was attributed to the improved light absorption and efficient charge separation at the interfaces of the Cu$_2$O dendrites, CuO nanowires and S-TiO$_2$ micro-blocks. Figure 13b shows a SEM image of the nanostructured photocatalyst, while Figure 13d displays the proposed band gap diagram, depicting the charge transfer mechanisms within the nanostructure.

![Figure 13. (a) Photocatalytic CH$_4$ evolution and (b) production rate employing various samples with varied ratios of ZnIn$_2$S$_4$ to TiO$_2$ (taken with permission from [75]). (c) SEM image of Cu$_2$O/S-TiO$_2$/CuO p-n-p nanostructure, and (d) band gap diagram with the mechanism involved in the conversion of CO$_2$ to CH$_4$ (taken with permission from [76]).](image)

The development of 3-D ordered macroporous TiO$_2$ (3DOM-TiO$_2$) is also an interesting strategy with the aim of improving photocatalytic CO$_2$ conversion. Furthermore, the loading of noble metals like Au, Ag and Pd onto 3DOM-TiO$_2$ results in an efficient photocatalyst nanostructure for improved conversion of CO$_2$ into useful chemicals. As previously reported, AuPd has an optimum ratio of 3:1 weight percent. This was loaded onto 3DOM-TiO$_2$, resulting in an enhanced CH$_4$ yield of 18.5 µmol/g h, whereas AuPd 1:3 exhibited an increased CO yield, 14 µmol/g h, when employing CO$_2$ and water vapors as reactants under UV visible light irradiation [77]. The key parameters responsible for the improved performance were deemed to be the increased light harvesting due to the slow photon effects of 3DOM-TiO$_2$ and the LSPR effect induced by the noble metals, and the efficient charge extraction at the interface of the noble metals and the semiconductors. Figure 14a represents the proposed mechanism for the photocatalytic conversion of CO$_2$ into CH$_4$ and CO when employing 3DOM-TiO$_2$ hierarchical nanostructures loaded with noble metals. Another study presented 3DOM-TiO$_2$ hierarchical nanostructures loaded with Au nanoparticles as an efficient photocatalyst...
for the conversion of CO$_2$ and water vapors into CH$_4$ under visible light irradiation [78]. The sample with the optimum Au loading exhibited an increased CH$_4$ yield (23.90 µmol/g h) as compared to the pristine sample (11.39 µmol/g h). This increase was attributed to the increased light harvesting due to the slow photon effect, the LSPR due to the uniformly loaded Au nanoparticles, and the effective charge separation at the interface between the Au nanoparticles and 3DOM-TiO$_2$. A representation of the proposed mechanism for the photocatalytic CO$_2$ conversion is depicted in Figure 14b.

![Proposed mechanism of photocatalytic CO$_2$ conversion with water vapors employing (a) AuPd-3DOM TiO$_2$ photocatalyst (taken with permission from [77]), and (b) Au-3DOM TiO$_2$ photocatalyst (taken with permission from [78]).](image)

**Figure 14.** Proposed mechanism of photocatalytic CO$_2$ conversion with water vapors employing (a) AuPd-3DOM TiO$_2$ photocatalyst (taken with permission from [77]), and (b) Au-3DOM TiO$_2$ photocatalyst (taken with permission from [78]).

6. Conclusions

The present review briefly reveals the influential and imperative aspects of TiO$_2$-based photocatalyst nanostructures, when applied for the purposes of photocatalytic CO$_2$ conversion. The recent developments in TiO$_2$-based nanostructures, i.e., 1-D, 2-D, and hierarchical nanostructures, have made it clear that, based on the geometry and configuration of the nanostructured photocatalyst, improved photocatalytic performance can be ascribed to a combination of (i) large surface areas, (ii) efficient separation of photogenerated charges, (iii) directional charge transport, (iv) improved light harvesting due to light trapping/scattering, and (v) the slow photon effect. Furthermore, the fabrication of hetero-junctioned nanostructured photocatalysts, coupled with noble metals, graphene derivatives, or another semiconductor, multiplies the photocatalytic performance, thus reaping the benefits of both, i.e., the aspects of both nanostructures and hetero-junction formation. Hence, it can be established that the unique and peculiar properties of nanostructured photocatalysts are accompanied by an improvement in photocatalytic performance, and their study is a potent research domain offering excellent prospects for photocatalytic conversion of CO$_2$ into value-added chemicals.

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