



Review article



Recent progress in TiO₂-Based photocatalysts for conversion of CO₂ to hydrocarbon fuels: A systematic review

Md. Arif Hossen^{a,b}, H.M. Solayman^c, Kah Hon Leong^d, Lan Ching Sim^e, Nurashikin Yaacof^c, Azrina Abd Aziz^{c,*}, Lihua Wu^f, Minhaj Uddin Monir^g

^a Faculty of Chemical and Process Engineering Technology, Universiti Malaysia Pahang, 26300, Gambang, Pahang, Malaysia

^b Center for Environmental Science & Engineering Research, Chittagong University of Engineering and Technology, 4349, Chattogram, Bangladesh

^c Faculty of Civil Engineering Technology, Universiti Malaysia Pahang, 26300, Gambang, Pahang, Malaysia

^d Department of Environmental Engineering, Faculty of Engineering and Green Technology, Universiti Tunku Abdul Rahman, 31900, Kampar, Perak, Malaysia

^e Department of Chemical Engineering, Lee Kong Chian Faculty of Engineering and Science, Universiti Tunku Abdul Rahman, 43200, Kajang, Selangor, Malaysia

^f Kuantan Sunny Scientific Collaboration Sdn. Bhd. Suites 7.23, 7th Floor, Imbi Plaza, Jalan Imbi, 55100, Kuala Lumpur, Malaysia

^g Department of Petroleum and Mining Engineering, Jashore University of Science and Technology, 7408, Jashore, Bangladesh

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ABSTRACT

Photocatalytic conversion of CO₂ by using sunlight and TiO₂ photocatalysts is a promising approach which produce hydrocarbon fuels to meet the future energy demands with hardly affecting the environment. This systematic review aims to provide rigorous overview of recent progress in TiO₂-based CO₂ photoreduction to produce hydrocarbon fuels along with future challenges. Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA) method was adopted to perform this systematic review. It uses explicit systematic approaches that are chosen to prevent bias, resulting in accurate data collection which helps to draw reliable conclusions. Peer-reviewed articles published in English language between year 2018–2022 were chosen from two main databases, namely Web of Science and Scopus. Depending on the search criteria 62 articles were selected for reviewing critically. Literature suggests that TiO₂-based photocatalysts have been increasingly used for reducing CO₂ to hydrocarbon fuels. Morphological alterations and surface modification techniques have been widely utilized to improve the photocatalytic performance and minimize limitations of pure TiO₂. Despite extensible efforts in this field, the utilization of hydrocarbon fuels still far away from practical applications. There are some challenges need to be addressed like environment friendly low-cost synthesis and modification method development, maximum visible light utilization, design of photoreactor with suitable product selectivity and kinetic model development for CO₂ reduction. This study portrays increased clarity regarding the advances and way forwards of crucial topics TiO₂-based CO₂ photoreduction. Such systematic review is crucial for researchers and academicians for setting future planning.

1. Introduction

Energy crisis and air pollution scenario of the world getting severe in recent years due to the increasing fuel consumption rate and rapid industrialization [1–3]. The U.S. Energy Information Administration (EIA) has predicted that by 2050, global energy consumption may increase by 50% [4]. Around 80% of the global energy demand is still fulfilled by using fossil fuels [5,6]. The key factor contributing to global warming and increasing greenhouse gases is the excessive burning of fossil fuels [7,8]. According to the United States Environmental Protection Agency (USEPA), CO₂ emission contributes roughly 80% of all

greenhouse gas emissions, and 65% of those emissions come from burning fossil fuels [9]. The world is gradually shifting to renewable energy sources for energy consumption considering the steady increase of CO₂ emission from fossil fuels combustion. Between 2017 and 2021, oil consumption declined by 2.75% each year, respectively, while renewable energy consumption increased by 4.85% per year (Fig. 1).

Solar energy is the most prevalent of the various types of renewable energy sources. Research and development strategies are going on to produce hydrocarbon fuels from CO₂ using solar energy. Photocatalytic production of hydrocarbon fuels from CO₂ is a viable technique for tackling global environmental issues while also ensuring future energy

* Corresponding author.

E-mail address: azrinaaziz@ump.edu.my (A. Abd Aziz).

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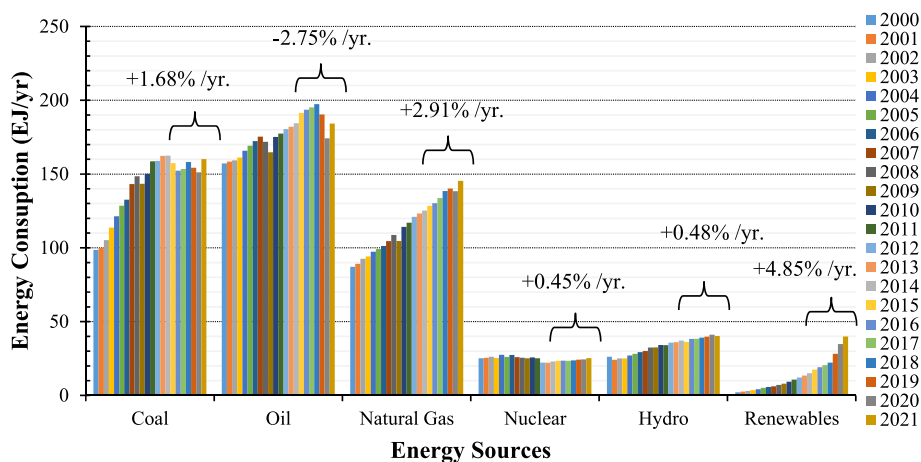


Fig. 1. Global energy consumption from various sources from 2000 to 2021 [10].

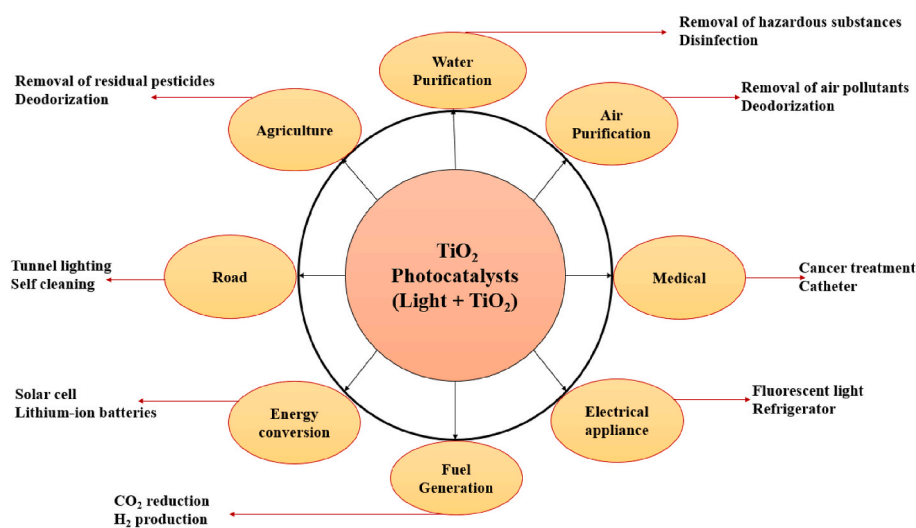


Fig. 2. Application of TiO₂-based photocatalysts.

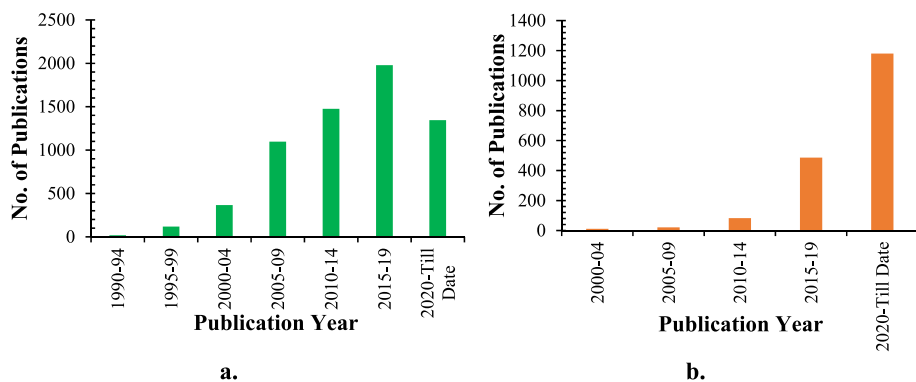


Fig. 3. Number of publications searching the terms: a) TiO₂ photocataly* or titanium dioxide photocataly*; and b) photocatalytic CO₂ reduction or photocatalytic CO₂ conversion or photocatalytic conversion of CO₂ or photocatalytic carbon dioxide reduction or photocatalytic carbon dioxide conversion or photocatalytic conversion of carbon dioxide. [Only journal articles (original and review) and conference papers included using Scopus database searched on November 15, 2022].

security [11]. Different semiconductor materials used as a photocatalyst in CO₂ photoreduction process. They are TiO₂, Cu₂O, ZnO, ZnS, CdTe CdS, CdSe, WO₃ and Bi₂WO₆ [12–15]. TiO₂ is the most used photocatalyst for its availability, stability, photoactivity and low toxic material properties [16,17]. Along with fuel generation TiO₂ has diverse

applications, as shown in Fig. 2. Since the discovery of TiO₂ as a photocatalyst by Fujishima and Honda, it has perceived a lot of attention as a possibility for CO₂ photoreduction into hydrocarbon fuels. Fig. 3 depicts the growing rate of publications dealing with TiO₂ photocatalysts and CO₂ photoreduction. There is a huge increase in number of studies

Table 1
Searching string used in this study and the total number of publications from two important databases.

Database	Searching String	Total	Combined
Scopus	TITLE-ABS-KEY ((“TiO ₂ ” OR “Titanium Dioxide” OR “TiO ₂ Photocataly*” OR “TiO ₂ Semiconductor”) AND (“CO ₂ ” OR “CO ₂ Reduction” OR “Carbon Dioxide Reduction” OR “Reduction of Carbon Dioxide” OR “Conversion of CO ₂ ”) AND (“Photocatalytic CO ₂ Reduction” OR “Photocatalytic Carbon Dioxide Reduction” OR “Photo-electrocatalytic Carbon Dioxide Reduction” OR “Photocatalytic Production of Solar Fuels” OR “Photocatalytic Production of Methane” OR “Carbon Dioxide to Methane” OR “CO ₂ to CH ₄ ” OR “CO ₂ to Hydrocarbon Fuels”))	337	853
Web of Science (WoS) core collection	TS=((“TiO ₂ ” OR “Titanium Dioxide” OR “TiO ₂ Photocataly*” OR “TiO ₂ Semiconductor”) AND (“CO ₂ ” OR “CO ₂ Reduction” OR “Carbon Dioxide Reduction” OR “Reduction of Carbon Dioxide” OR “Conversion of CO ₂ ”) AND (“Photocatalytic CO ₂ Reduction” OR “Photocatalytic Carbon Dioxide Reduction” OR “Photo-electrocatalytic Carbon Dioxide Reduction” OR “Photocatalytic Production of Solar Fuels” OR “Photocatalytic Production of Methane” OR “Carbon Dioxide to Methane” OR “CO ₂ to CH ₄ ” OR “CO ₂ to Hydrocarbon Fuels”))	707	

Note: The data here includes reviewed and original articles of all languages.

considering photocatalytic CO₂ reduction in the last three years (Fig. 3b).

TiO₂ is the most affordable, readily useable, and well-characterized UV light active semiconductor photocatalyst. However, practical applications of TiO₂ are greatly hindered by its wide inherent band gap (E_g = 3.2 eV for anatase), quick recombination of photogenerated charges, and low solar light utilization (about 5%) [18,19]. Therefore, considering practical standpoint, it is crucial to increase the capacity of TiO₂ for light absorption and electron-hole separation efficiency. Nevertheless, CO₂ is a highly stable molecule ($\Delta G^\circ = -400 \text{ kJ mol}^{-1}$) with linear symmetrical configuration, fully oxidized carbon, and an average carbon-oxygen double bond energy of up to 804.4 kJ mol⁻¹ (at 298 K) [20]. Thus, strong photocatalyst is required to convert it into value-added chemicals. TiO₂ produces electron and holes when exposed to UV light, which aids in the dissociation of CO₂ bonds. The rate at which CO₂ breakdown will depend on how quickly electron-holes are generated. Improvement of charge separation efficiency and enhancement of visible light absorption can be attributed TiO₂ as strong photocatalyst to convert CO₂ [21]. Along with morphological modification, most widely used approaches to produce highly effective TiO₂ for CO₂ photoreduction is the modification of TiO₂ surface by using metal deposition, metal doping, non-metal doping, dispersion on supports, carbon-based materials doping, surface sensitization and heterojunction methods [22,23].

With increasing research investigating to improve CO₂ photoreduction performance of TiO₂-based photocatalysts, summarizing those findings systematically is deemed crucial. Some descriptive review works on TiO₂-based CO₂ photoreduction have been done [7,22,24], as far as our knowledge there is no systematic review performed. Systematic review offers a structured overview on a particular topic that aids academics and researchers in keeping updated with the literature [25]. The purpose of this paper is to systematically summarize the recent advances with future challenges of TiO₂-based photocatalysts for conversion of CO₂ to hydrocarbon fuels. Particularly, various modification

techniques of TiO₂ to enhance CO₂ photoreduction are extensively discussed. Moreover, great importance is also given to providing deeper understanding on factors affecting the CO₂ photoreduction performance. Finally, future challenges and way forwards for practical applications of TiO₂ photocatalysts for CO₂ photoreduction are described.

2. Methods

This work was driven by investigating recent progress and future challenges of TiO₂-based photocatalysts for photoreduction of CO₂ to hydrocarbon fuels. In order to fully understand the current progress and impending challenges we explored the recent literature as the primary source. Preferred Reporting Items for Systematic Reviews and Meta-Analyses (PRISMA), a well-known published protocol to perform a systematic literature review was used in this study. This method uses very clear and systematic approaches that are specifically chosen to avoid bias, resulting in accurate information gathering which leads to create trustworthy conclusions.

2.1. Literature search process

The present study was carried out utilizing two key databases, Scopus and Web of Science (WoS) along with other sources, because both databases are reliable and cover more than 256 areas of study, including environmental fields [26]. We formulated a search string based on our understanding and knowledge in relevant field. The search string used in this study tabulated in Table 1. The literature was searched using advanced search options in both databases. First, we queried both database in early June 2022 and second time on the November 15, 2022, for getting maximum publications in the year 2022. Fig. 4 depicts the general screening methods and the flow of identifying relevant publications for reviewing. In the identification stage 337 articles from Scopus, 707 articles from WoS database and 171 articles from other sources were retrieved. When researchers retrieve publications from two or more databases using the same library format, merging the articles from databases to undertake unique analyses might be difficult, particularly when the databases are large. In this study unique technique suggested by Echchakoui [27] to merge publications of all databases was used. In the screening process, total of 201, articles were excluded due to duplication in both databases. Inclusion and exclusion criteria were set to further refine the 1014 results obtained after removing replicate and merging both articles of both databases.

2.2. Eligibility criteria

We refined our results by only considering exclusion criteria: (i) review articles; (ii) book series & book chapter; (iii) conference proceedings; (iv) non-English language; (v) published before year 2018; (vi) meta-analysis & articles in press; and (vii) articles not open access & access by UMP library. After considering the articles based on inclusion and exclusion criteria, 102 studies remained in eligibility stage. A database with the 102 articles containing titles, abstracts and full texts was created in Mendeley reference management software. More importantly, at this step, all of the papers' titles, abstracts, and contents were carefully scrutinized to make sure they met the inclusion requirements and were appropriate for use in the current study in order to fulfil the objectives. Consequently, a total of 40 articles were excluded because they are not based on empirical data and focused on TiO₂-based photoactivity. Finally, total 62 remaining articles were selected to analyze.

3. Results

3.1. Overview of the selected studies

Research on photocatalytic CO₂ reduction to produce hydrocarbon

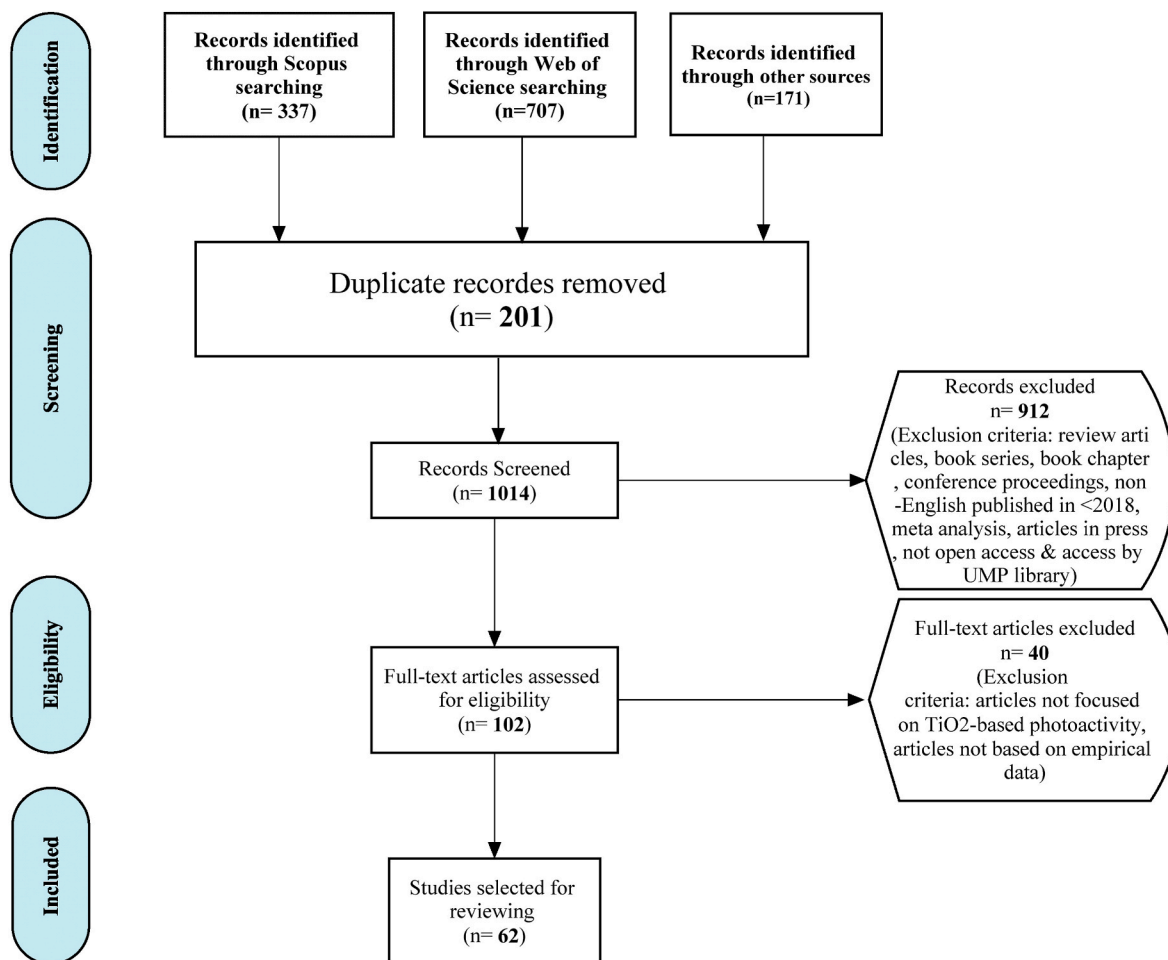


Fig. 4. Flowchart of study based on the PRISMA recommended protocol.

fuels using TiO₂-based photocatalysts has been increasing for getting alternative options to reduce pressure on fossil fuels. In this review, 62 articles from 17 different countries of the world were selected based on the criteria depicted in Fig. 4. The largest number of studies were carried out in Asian region (Fig. 5a). The highest around 42% (n = 26) of studies reviewed were conducted in China (Fig. 5b). All articles selected for this study were published between 2018 and 2022. Fig. 5c exhibits year wise selected publications number. About 60% (n = 37) of studies reviewed were published between 2020 and 2021. The articles reviewed were obtained from 36 different journals including nine (09) publishers. Most of these journals were published in the subject areas of chemical engineering, materials science, environmental science, chemistry, and energy.

3.2. Recent progress of TiO₂-based photocatalysis

Titanium dioxide (TiO₂) is the most studied semiconductor photocatalysts, and it has been utilized remarkably in the field of environmental purification and energy generation. It is worth mentioning that almost two third of the recent publications on photocatalysis utilizing TiO₂ as a photocatalyst which shown in Fig. 6. When exposed to a photon with an energy equivalent to or more than its bandgap, TiO₂ can produce electron-hole pairs. Based on the specific electronic pathway maintained by a certain species, the disposition of photogenerated electrons (e_{CB}^-) and holes (h_{VB}^+) may be identified [28]. Typical reaction mechanism involved in photocatalytic processes and approach in CO₂ photoreduction is illustrated in Fig. 7a, b. The discharge of heat occurs when the input energy is depleted.

Generally, appropriate semiconductor is classified by three key characteristics: firstly, the bandgap energy (E_g), secondly, the locations of conduction band (CB) and valence band (VB), and thirdly, the behaviors of photogenerated electrons and holes [28,31]. The rates of interface charge recombination and interfacial charge carrier are the important behaviors of photogenerated electrons and holes [32]. One of the fundamental barriers to the practical application of TiO₂ photocatalysts is charge recombination at deep level defects, which reduces TiO₂'s photocatalytic performance [33–36]. Yu et al. [36] proposes a method that employs shallow-level defects thermally stimulating the migration of trapped electrons above the deep-level defects via solution plasma processing (SPP) technology. Semiconductor photocatalysts with $E_g > 3.0$ eV, for example, are solely active in UV light, while those with $E_g < 3.0$ eV are more effective in visible light. The band positions of mostly used semiconductors (such as TiO₂, Cu₂O, CdSe, ZnO, CdS, WO₃ and Bi₂WO₆) and redox potentials versus (vs.) Normal Hydrogen Electrode (NHE) of CO₂ reduction at pH = 7 are shown in Fig. 7c. The association between band energy and the redox potential of the product selectivity determines the types of compounds that can be created from the process [37]. The redox potential and band gap relationship also applies to CO₂ reduction to various hydrocarbon fuels, such as CH₃OH, HCOOH, and CH₄. Both TiO₂ and ZnO, which are widely used photocatalysts, have advantages and disadvantages. Use of TiO₂ instead of ZnO can be favorable in terms of bandgap, cost, stability, and many other characteristics. Since its discovery in 1972, researchers have been attempting to extract the photocatalytic benefits of TiO₂ as well as solutions to its drawbacks.

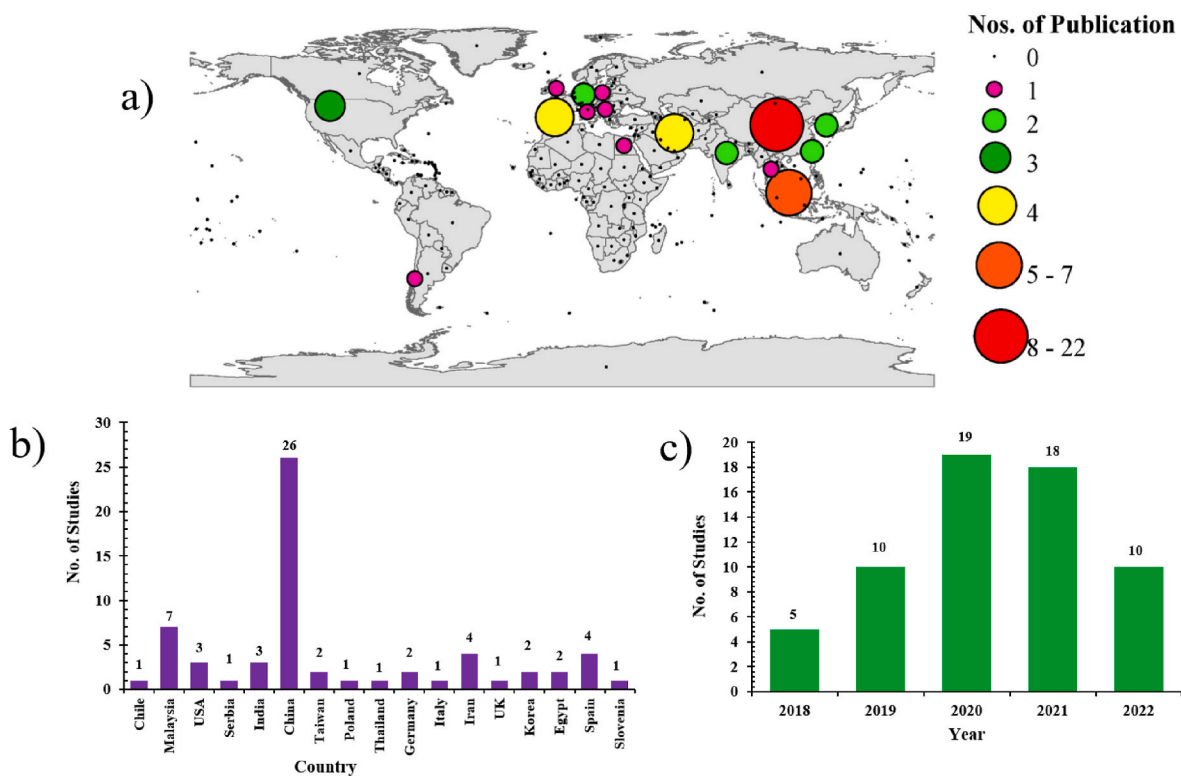


Fig. 5. Number of studies reviewed from specific countries: a) projected in the world map, b) projected in a bar chart and c) year-wise selected studies.

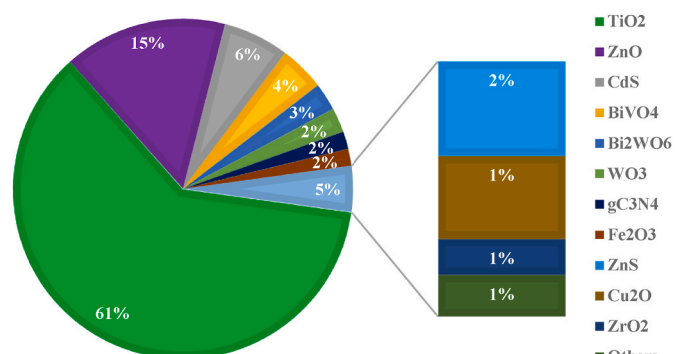


Fig. 6. Recent publications on photocatalysis utilizing different semiconductors from 2018 to 2022. (Publications search by using Scopus database).

3.3. Factors affecting the photocatalytic activity of TiO₂-based photocatalysts

3.3.1. Particle size and shape of the photocatalysts

The photocatalytic performance of a catalyst is comprehensively affected by the particle size and shape of the catalyst because a catalyst with small particle size and desired shape holds sufficient surface-active sites and there is a more possibility to promote the interfacial charge separation [31]. The synthesis methods of photocatalysts have significant influences on their morphology [38]. Sol-gel, template assisted synthesis, hydrothermal treatment and electrochemical anodization are frequently used methods for the synthesis of TiO₂ nanostructures. Among these methods electrochemical anodization allows for the development of self-organized TiO₂ nanostructures with low cost and simplicity of geometry control (length, diameter, and wall thickness) by the use of appropriate anodization parameters [39]. It has been revealed that TiO₂ nanoparticles showed better photocatalytic performance than that of TiO₂ microparticles, which can be attributed to their smaller

diameter [40]. The travel distance required for photogenerated charge carriers are shortened when particle size decreases, hence, lowering charge recombination. Li et al. [41] investigated the consequences of particle size on the morphology and photocatalytic activity by alkali treated TiO₂. By varying the alkali-hydrothermal duration (0–48 h), TiO₂ nanoparticles with various crystalline sizes were produced by them. Among the prepared samples, pore volume of TiO₂-24 was found maximum with minimum pore diameter. The XPS spectrum of TiO₂-X showed TiO₂-24 had lower intensity versus binding energy curve. TiO₂-24 nanoparticles exhibited better photocatalytic performance under visible light was due to the collective impacts of surfaces defects and crystalline size.

The morphology (shape) of nanoparticles has also influenced on the improvement of photocatalytic performance. The electron-hole recombination in nanotube (NT) shaped photocatalyst is greatly retarded because photogenerated electrons need to travel vectorially along the NT wall. For instance, Huang et al. [42] constructed one dimensional TiO₂ nanostructures through a single-step hydrothermal method. Results revealed that one dimensional (1D) TiO₂ nanostructures catalysts had a high specific surface area, improved photocatalytic CO₂ reduction. Methane was produced at highest yields of 19.16 and 12.71 μmol/g over the TiO₂ nanotubes (TNT) and nanorods (TNR), respectively, which were approximately 2.33 and 1.48 times higher than TiO₂ nanoparticles (TNP). The effect of facet on TiO₂ nanostructures and their photocatalytic performance was investigated by Kowalkińska et al. [43]. They noted that TiO₂ with octahedra exposing {101} facets had the maximum photoactivity and mineralization efficiency when exposed to UV-vis light, with these properties decreasing as subsequent facets develop and are exposed more.

3.3.2. Surface area of the photocatalysts

Besides, morphology (shape, size) control of TiO₂, the increase of specific surface area is another promising approach to achieve photocatalytic activity improvement. The surface area of nanoparticles depends on their porosity and particle size [44]. One dimensional TiO₂

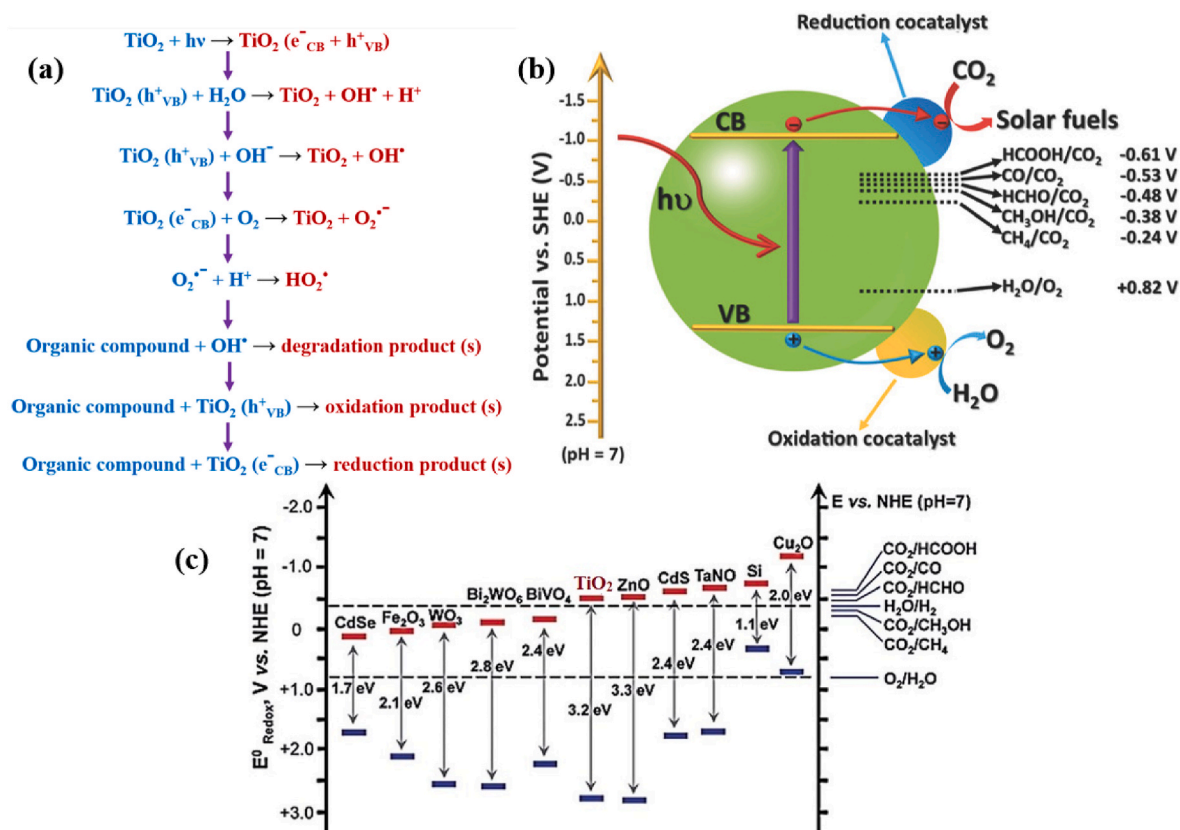


Fig. 7. (a) Mechanism involved in photocatalytic process (b) Typical approach in CO₂ photoreduction and (c) Band positions of certain semiconductors in relation to CO₂ reduction energy levels (Reproduced from Refs. [28,29,30] with permission).

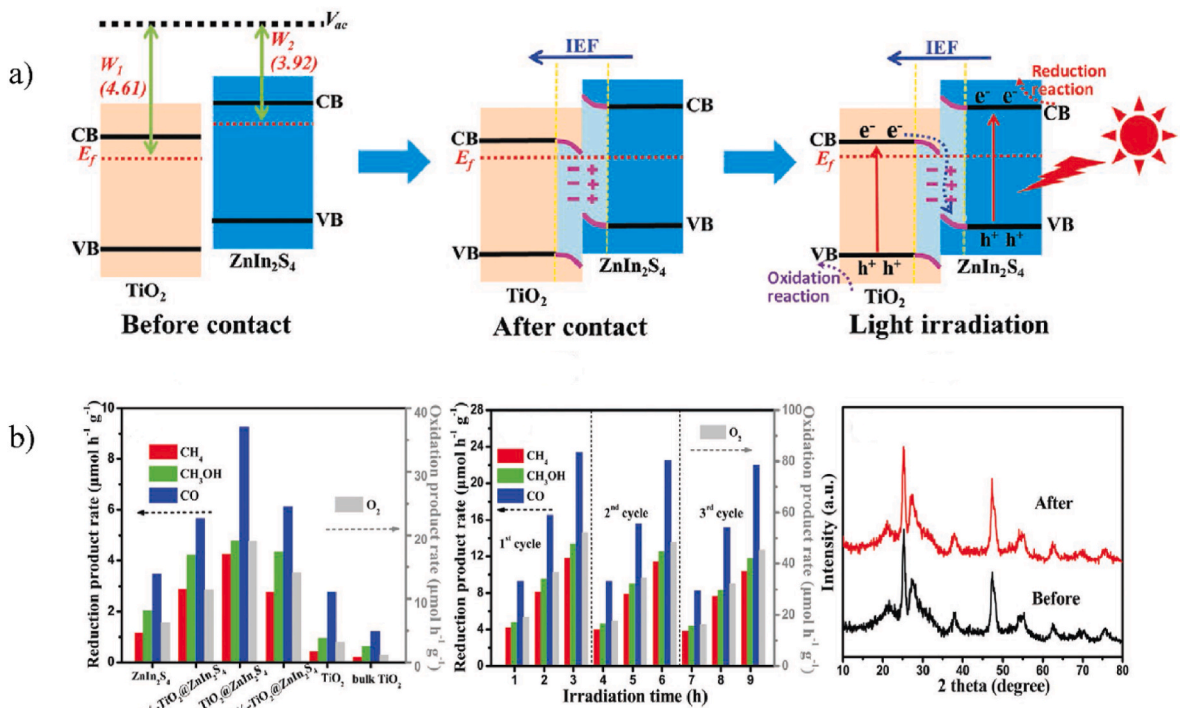


Fig. 8. Influence of specific surface area on enhancement of photocatalytic CO₂ reduction (a) illustration of the S-scheme transfer process between TiO₂ and ZnIn₂S₄ and (b) Yield of products in photocatalytic CO₂ reduction (PCR) reaction of different samples with stability tests (Adopted from Ref. [47] with prior permission from Wiley Publisher).

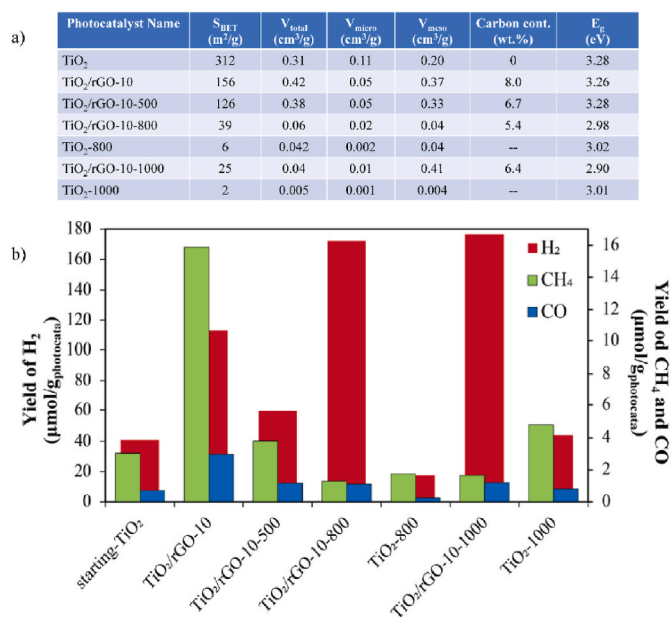


Fig. 9. Effect of calcination temperature (a) properties of photocatalysts and (b) products yield of tested photocatalysts during CO₂ photoreduction with H₂O (Reproduced from Ref. [50] with due permission from Elsevier).

nanostructures, especially, TNT has a high specific surface area and higher rate of photocatalytic CO₂ reduction ability than other nanostructures [42]. Due to the tubular shape and length, TNT intrinsically offer a high surface area [45]. Das et al. [46] explored a hierarchical ZnO–TiO₂ heterojunction strategy-driven technique to enhance photocatalytic performance by combining enhanced surface area and interfacial charge carrier. They reported that combining structural tuning with heterojunction leads to enhanced surface area and useful charge carrier separation, which improves photocatalytic activity. Wang et al. [47] investigated S-Scheme TiO₂@ZnIn₂S₄ photocatalyst for successful CO₂ photoreduction as shown in Fig. 8. The results indicated that improvement of photocatalytic CO₂ reduction is ascribed to the enlarge specific surface areas with sufficient active sites. When the TiO₂@ZnIn₂S₄ heterojunction is subjected to light, electrons are excited and easily move to the VB of ZnIn₂S₄ and recombine with the photo-generated holes of ZnIn₂S₄ due to the interface band bending and Coulomb interaction (Fig. 8a). As illustrated in Fig. 8b, the main photoreduction products of samples are CO, CH₃OH, and CH₄. In particular, when compared to pristine ZnIn₂S₄ and TiO₂, the overall CO₂ photoreduction conversion rates of the examined S-Scheme TiO₂@ZnIn₂S₄ photocatalyst enhanced by 2.75 and 4.43 times, respectively, reaching 18.32 μmol h⁻¹ g⁻¹.

3.3.3. Calcination temperature

Calcination refers to the process of heating a material to a high temperature that is lower than the melting point. It significantly affects the produced photocatalysts' morphology, crystallinity, surface area, pore-volume, and phase structure, which influences the photocatalytic performance as well. Wu et al. [48] decorated Pd-calcined black TiO₂ nanoparticles in an argon environment using the sol-gel method. At various calcination temperatures, the synthesized photocatalyst was examined, and the maximum behavior was recorded photocatalyst calcined at 400 °C. In another study, Phromma et al. [49] investigated particle size, crystallite size, and phase separation of TiO₂ nanoparticles to determine the impact of calcination temperature on photocatalytic activity. The results showed that anatase had a significant impact on photocatalytic activity between 300 and 600 °C, however the particle size of TiO₂ was shown to have a dominant impact between 600 and 700 °C. Morawski et al. [50] examined the effect of

calcination temperature on TiO₂/rGO for the CO₂ photoreduction. Above 500 °C calcined temperature substantial reduction of band gap energy and BET surface area was observed (Fig. 9a). This is due to the aggregation of TiO₂ particles during calcination and incorporation of rGO in composite. The highest yield for CH₄ and CO production was observed for TiO₂/rGO-10 without calcination, followed by H₂ calcined at 1000 °C (Fig. 9b).

3.3.4. Photocatalytic reactors

The efficiency of photocatalytic CO₂ reduction is substantially influenced by the photocatalytic reactors utilized [51]. In most cases, CO₂ photoreduction is performed in either batch or continuous-flow mode reactor systems. For the case of batch type reactors, product accumulation and re-adsorption, as well as additional reverse or side reactions, are always a possibility [11]. Overall, batch type reactors are not a suitable choice for long-term or large-scale applications. Alternatively, continuous-flow type reactor systems can improve the aforementioned issues in batch type reactors [52]. Dilla et al. [53] constructed a tubular continuous flow reactor to improve the interaction between gaseous CO₂ reactants and the TiO₂ photocatalyst surface, allowing the approach to be used on a larger scale and in industrial application.

It is indispensable to ensure that the photocatalyst is illuminated to its maximum extent and comprehensive interaction of reactants occurs with the photocatalyst surface. In general, this entails two approaches: increasing the catalyst surface area and increasing the quantity of light incident on the reactor. A monolith photoreactor was constructed on a continuous photocatalytic reactor by Tahir [54] after loading the TiO₂ photocatalyst over structured 3D MAX Ti₃AlC₂. The higher yield rate of CO, H₂ and C₂H₆ with good stability was observed using the monolith photoreactor in comparison with the fixed bed photoreactor (Fig. 10). Higher photocatalytic conversion rate was reported due to the lighted surface area to volume of the monolith photoreactor, high flow rates, decreased pressure drop, increased catalyst loading, and efficient exploitation of photon energy. Giusi et al. [55] developed a unique gas progression photocatalytic reactor relying on copper-functionalized nanomembranes for CO₂ photoreduction. They used a concept that was substantially distinct from traditional photocatalytic methods. It was possible to demonstrate for the first time the extremely selective CO₂ conversion to C1–C2 carboxylic acids without production of H₂, CO, CH₄, or other hydrocarbons due to the unique properties and conditions of the photoreactor.

3.4. Modification techniques to enhance the photocatalytic CO₂ reduction

TiO₂ photocatalysts received noteworthy attention in the field of CO₂ reduction reactions as they are readily available, affordable, stable, and environmentally safe. However, the two key problems preventing practical use are the restricted ability to absorb in the visible light spectrum and the quick recombination of photogenerated electrons and holes [56,57]. Through surface modifications, the properties of photocatalytic materials can be changed significantly, which provides the possibility to improve photocatalytic activity and even induces new photocatalytic reaction paths. In this section, the latest research progress of surface modifications techniques to improve the CO₂ photoreduction performance will be discussed. Several surface modification strategies as shown in Fig. 11 have been used overcome the drawbacks of TiO₂ and enhancing the CO₂ photoreduction.

3.4.1. Metal deposition

Metal deposition is an appealing approach to enhance the photocatalytic activity of TiO₂ nanocomposites. Although metal deposition is an expensive modification method, it significantly enhances electron–hole separation in semiconductor materials [22]. The ability of metals to accept photogenerated electrons improves as the working functionality of the metal increases. Consequently, it improves the electron–hole

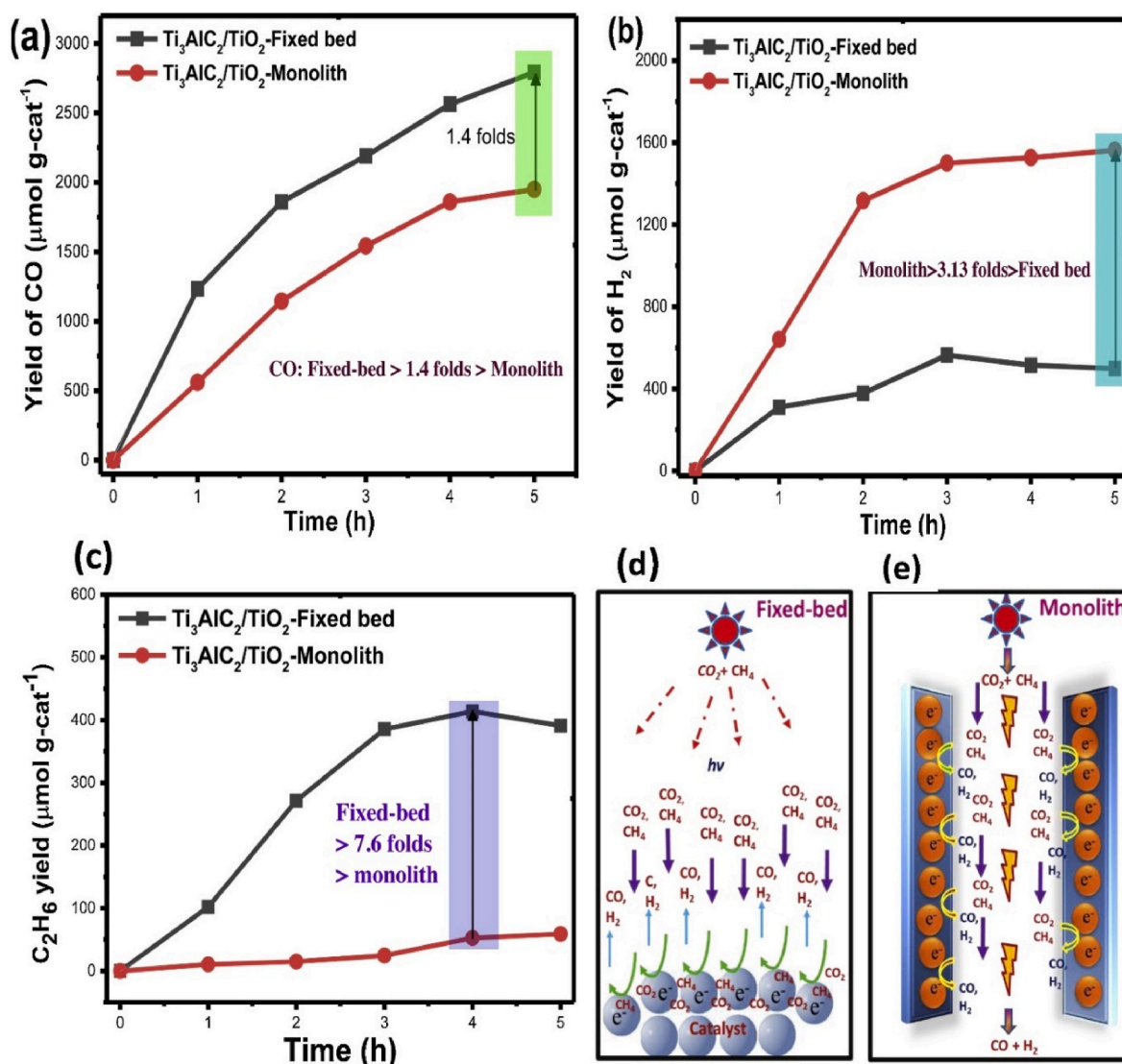


Fig. 10. Evaluation of CO_2 photoreduction activity of fixed bed and monolith type photoreactor: (a) production of CO; (b) production of H_2 ; (c) production of C_2H_6 ; (d) process of fixed bed type reactor and (e) process of monolith type photoreactor system (Adopted from Ref. [54] with permission from Elsevier).

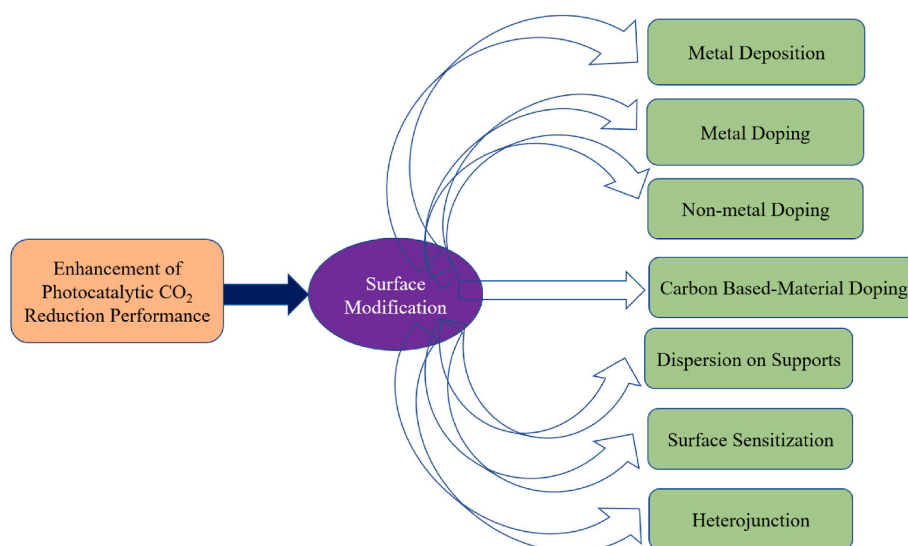


Fig. 11. Modification techniques to improve the CO_2 photoreduction performance.

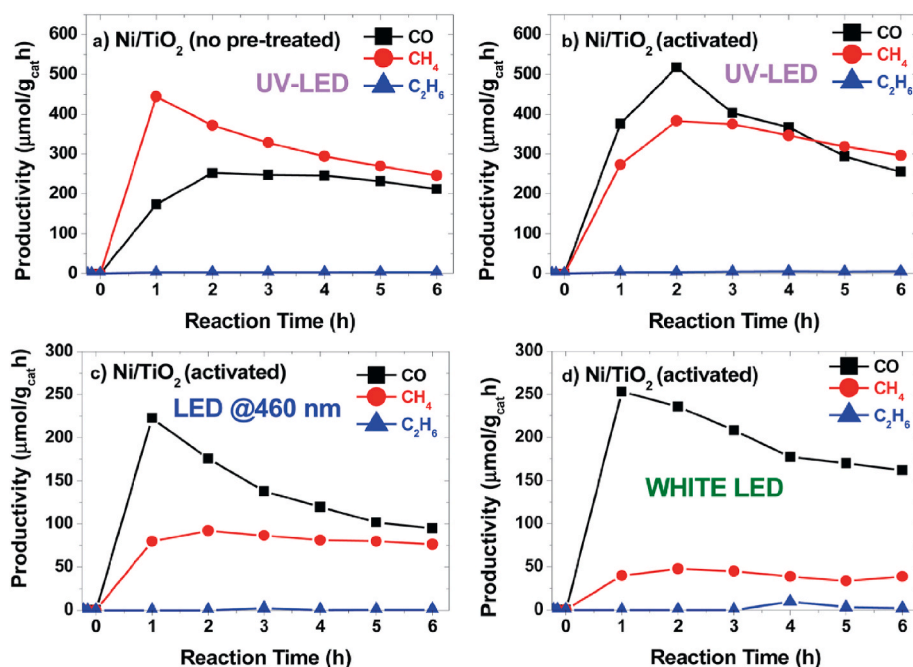


Fig. 12. Productivity of different products for Ni/TiO₂ catalyst under LED light irradiation (a) at 365 nm untreated, (b) at 365 nm activated, (c) at 460 nm and (d) white light (Adopted from Ref. [60] with permission from Royal Society of Chemistry).

separation, hence enhances the overall photocatalytic performance of TiO₂. The absorption edge of TiO₂ is reduced when low bandgap energy metals are deposited, adjusting the visible light response [7]. Platinum (Pt), palladium (Pd), copper (Cu), nickel (Ni), gold (Au), and silver (Ag) are some of the most typically deposited metals. Devi et al. [58] used Pt-coated GO wrapped TNTs to increase CH₄ production by CO₂ photoreduction at a moderate temperature and pressure. They have successfully produced CH₄ at a high rate of 3.42 mmol g⁻¹ h⁻¹. Reñones et al. [59] performed a study on Au–Ag deposited TiO₂ photocatalysts for CO₂ reduction. Compared to only producing syngas over pure TiO₂, the results showed that bimetallic catalysts can alter the reaction selectivity into CH₄ under UV light irradiation. Sanz-Marco et al. [60] examined Ni deposited LED-driven TiO₂ for visible-light expanded conversion of CO₂. The photocatalytic conversion of CO₂ into CO, CH₄ and C₂H₆ alkanes was examined under LED irradiation at different wavelengths (Fig. 12). Results showed that when Ni/TiO₂ catalysts were illuminated at 365 nm, maximal productivity of CH₄ was 450 mmol g⁻¹ h⁻¹ and CO was 250 mmol g⁻¹ h⁻¹, with C₂H₆ production being nearly constant throughout the process, reaching roughly 2 mmol g⁻¹ h⁻¹. Under the visible region of the solar spectrum the productivity of CO increased significantly compared to CH₄ and C₂H₆ (Fig. 12c and d). Liu et al. [61] studied the performance of CO₂ photoreduction by implying Cu deposition on different TiO₂ substrates. It was revealed that both

TiO₂@Cu and H–TiO₂@Cu showed exceptional improvement for CO and CH₄ production. Another important finding was also found from the study that not only synthesis technique significantly enhances the CO₂ reduction activity after Cu deposition, however the substrate utilized for loading and the chemical state of inserted material will also affect the following catalytic activity. Recently, Zhan et al. [62] examined Pd nanoparticles on surface of TiO₂ for enhancing photocatalytic reduction of CO₂ to CH₄. The Pd–HN–TiO₂ composite, which contains Pd, was synthesized by coordinating Pd(OAc)₂ with *N*-heterocyclic carbene in the skeleton, while HN serving as a platform to link TiO₂ with extensively dispersed Pd nanoparticles and increase CO₂ adsorption. Results showed that with a progress rate of 237.4 mol g⁻¹ h⁻¹ and selectivity of more than 99.9%, this composite with a surface area of 373 m² g⁻¹ improves CO₂ photoreduction efficiency to CH₄. Pure TiO₂, HN had a low CO₂ reduction efficiency for CH₄ and CO production, however the evolution rate of CH₄ increased somewhat after loading with Pd, while the rate of CO remained almost constant.

The visible-light activity of various semiconductor materials has been reported to be improved by Au and Ag nanoparticles deposition due to the effects of localized surface plasmon resonance (LSPR) and Schottky barrier development. With regard to the LSPR, an electromagnetic field is developed, and the photoreaction is enhanced through scattered photons, plasmonic energy transfer and electron excitation

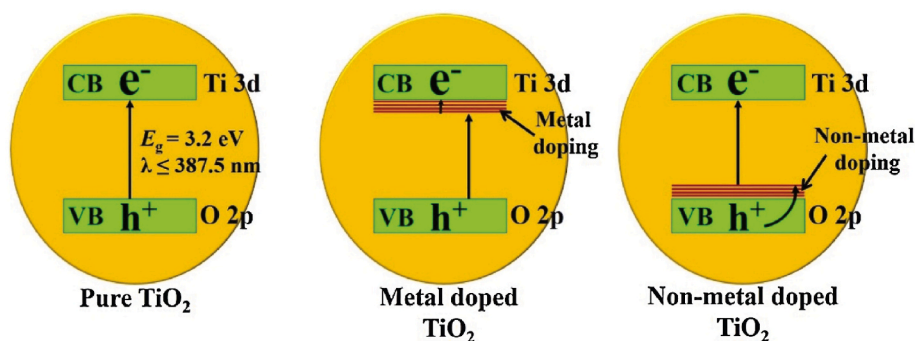


Fig. 13. Schematic illustration of band structure of the pure, metal doped and non-metal doped TiO₂ (Adopted from Ref. [68] with permission from Elsevier).

Table 2
Summary of recent photocatalytic CO₂ reductions using metal doping.

Photocatalyst	Reductant	Photoreactor	Type of light	Product	Yield ($\mu\text{mol g}^{-1} \text{h}^{-1}$)	References
Pt-Ru/TiO ₂	CO ₂ +H ₂ O	Gas-closed circulation system	Xe lamp (320–780 nm)	CH ₄	38.7	[69]
Fe/TiO ₂	CO ₂ + H ₂	Continuous flow quartz	Hg lamp (252 nm)	CO	166	[70]
Ag/TiO ₂	CO ₂ +H ₂ O	Continuous flow reactor	Xe lamp (365 nm)	CH ₄	0.42	[71]
				C ₂ H ₆	0.10	
				CH ₃ OH	1.9	
Ni-Bi/TiO ₂	CO ₂ +H ₂ O	Batch photo-reactor	Hg lamp (350 nm)	CH ₄	2.4	[67]
Cu/Cu+@TiO ₂	CO ₂ + Na ₂ SO ₄	Quartz	Xe lamp (350 nm)	CH ₄	21.1	[72]
Ag/TiO ₂	NaHCO ₃ + H ₂ O	Photochemical reactor	Hg lamp (350 nm)	CO	1.9	[73]
				CO	11.5	
				C ₂ H ₆	28.8	
Pt-Au/R-TNTs	CO ₂ +H ₂ O	Quartz cell	LED light source (365 nm)	C ₂ H ₆	28.8	[74]
Pd/TiO ₂ -N	CO ₂ + NaHCO ₃	Quartz cell	Hg lamp (320–390 nm)	CH ₄	360.0	[75]
				C ₂ H ₄	9.2	
Pt/TiO ₂ -N	CO ₂ +H ₂ O	Continuous flow reactor	LED light (365–530 nm)	CO	8.3	[76]
					8.8	
Au/TiO ₂ (Ar)	CO ₂ +H ₂ O	Reactor	Xe lamp (320 nm)	CH ₄	3.9	[77]
				C ₂ H ₆	0.87	
				CH ₄	31.6	

[63]. However, the development of a Schottky barrier increases photoactivity by trapping and extending the lifetime of the electrons. Khatun et al. [64] deposited Au nanoparticles in the TiO₂ nanotube by simple electrochemical deposition method to improve CO₂ photoreduction to CH₄. Light harvesting properties of prepared Au-TNTs catalysts showed improvement under visible light owing to its LSPR behavior. The photocatalytic performance of TNTs and Au-TNTs increased considerably, yielding of 8.26% and 14.67% higher CH₄ production than bare TiO₂, respectively. In another study, Feng et al. [63] demonstrated the photo-deposited Ag nanoparticles at two orders: MgO deposition followed by Ag (Ag/MgO/TiO₂) and Ag deposition followed by MgO (MgO/Ag/TiO₂) to improve the performance of CO₂ photoreduction. They revealed that the Ag/MgO/TiO₂ catalyst with seven deposited atomic layers of MgO and 5% Ag was 14-fold more active compared to pure TiO₂ for CO and CH₄ production. Li et al. [65] studied the photo-thermal catalytic performance of TiO_{2-x}/CoO_x photocatalysts for enhancing CO₂ photoreduction. The demonstrated 175 times yield of CH₄ than bare TiO₂ under UV irradiation at elevated temperature.

3.4.2. Metal doping

Metal doping is the most extensively used surface modification approach for preventing photogenerated electron-hole pairs from recombining on TiO₂ surface [22,66]. Pure TiO₂ is not able to absorb high photon energy due to its high band gap energy (3.2 eV), however doping reduces the band gap energy (Fig. 13). The addition of metal nanoparticles in the TiO₂ matrix causes structural defects and decreases the TiO₂ bandgap, lowering the absorption threshold to visible levels [22]. Nematollahi et al. [67] reported that incorporation of Ni and Bi gradually decreased band gap energy compared to pristine TiO₂ from 3.1 to 2.84 eV. Ni-Bi doped TiO₂ exhibited 6.5-fold more yield of CH₄ compared to pristine TiO₂. In diverse investigations, Pt, Au, Ag, Fe, Cu, Ni, Pd, and Ru have been doped in TiO₂ matrix and shown to enhance its photocatalytic performance (Table 2).

In the case of a doped photocatalyst, photoreduction of CO₂ occurs on the surface of doped metal atoms. When photoexcitation happens, electrons are transmitted to the conduction band from valence band, subsequently these electrons are again moved to the metal heteroatom,

resulting in CO₂ conversion. Pan et al. [74] examined a binary component catalyst composed of single atoms (SAs- Pt and Au) which fixed on self-doped TNTs for CO₂ photoreduction. The results showed that the covalent interactions enabled an effective transfer of photogenerated electrons from the defect sites to the SAs, thereby improving separation of electron-holes and transfer of charge carrier. The maximum photocatalytic performance of Pt-Au/R-TNTs with 0.33 wt% single atom metals was recorded 149 times that of unmodified R-TNT, with yields of CH₄ and C₂H₆ attained to 360.0 and 28.8 $\mu\text{mol g}^{-1} \text{h}^{-1}$, respectively. Table 2 provided information on several metal-doped TiO₂-based photocatalysts, associated experimental conditions, and CO₂ photoreduction performance. It is observed from the Table 2, the yield of CO₂ converted products is highly dependent on metal selection, reductant employed, photoreactor, source and intensity of light irradiation, and product selectivity. Tahir [70] investigated the performance of structured montmorillonite (MMT)-loaded Fe-doped TiO₂ (Fe/TiO₂) nanocomposite for dynamic photoinduced CO₂ reduction to fuels using H₂ as the reductant. The results of the study showed that the photoactivity and stability of the Fe-MMT/TiO₂ catalyst for the generation of hydrocarbon fuels using the monolithic photoreactor was significantly enhanced in comparison to the cell-type reactor. Jin et al. [75] reported how to choose the appropriate metal cocatalysts in combination with TiO₂'s surface basicity to improve photocatalytic CO₂ reduction efficiency. Uniform ligand-free metal nanoparticles of Ag, Cu, Au, Pd, and Pt doped on TiO₂ surfaces were investigated for CO₂ photoreduction utilizing water as the reductant. According to reported results, Ag is most active in producing CO, although Pd and Pt primarily generate hydrocarbons like methane and ethane, and amine-modified TiO₂ has a 2.4-fold enhancement in CO₂ photoreduction performance compared to TiO₂ without amines. Recently, Zhou et al. [77] investigated the performance of CO₂ photoreduction into CH₄ over Ru-doped TiO₂. Improvement of CO₂ photoreduction to CH₄ was aided by the synergistic influence of Ru and oxygen vacancies. The optimum Ru-doped TiO₂ (1% Ru-TiO_{2-x}) showed a substantial increase in photocatalytic activity, which is much greater than Ru-TiO₂ and TiO_{2-x}, with a CH₄ yield of 31.6 $\mu\text{mol g}^{-1} \text{h}^{-1}$.

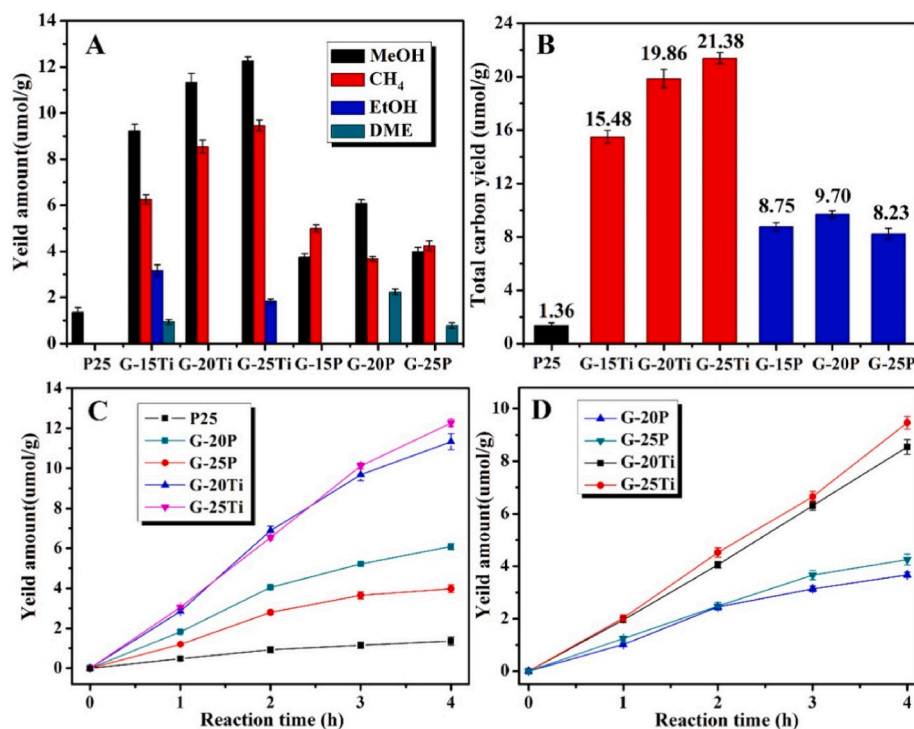


Fig. 14. Effects of reduced graphene oxide modified TiO₂ composites on photocatalytic CO₂ reduction (a) yields of MeOH, CH₄, EtOH, and DME; (b) total carbon yields of CO₂ photoreduction for distinct catalysts; (c) yields rate of MeOH and (d) CH₄ (Taken from Ref. [90] with permission Elsevier).

3.4.3. Non-metal doping

Another type of surface modification approach of TiO₂ is non-metals doping. Non-metal doping has been used to improve the spectrum sensitivity of TiO₂ composites in a similar way to metal doping. As illustrated in Fig. 13, non-metals dopants lower the bandgap of TiO₂ by adding new energy levels above VB and enable electron excitation from VB to CB. Nonmetal dopants such as N, C, S, and P are often applied to reduce the TiO₂ band gap and hence increase the absorption of visible light [22,78]. Nor & Amin [79] investigated glucose precursor C-doped TiO₂ for improving CO₂ photoreduction efficiency to produce CH₃OH. The photocatalytic performance of C-doped TiO₂ was recorded highest with 6 wt% glucose loading (6C-TiO₂), with a CH₃OH yield of 19.5 mmol g⁻¹ h⁻¹, which is 2-fold higher than pure TiO₂ at 9.5 mmol g⁻¹ h⁻¹. The computed E_{CB} for TiO₂ was 0.41 eV and for 6C-TiO₂ was 0.27 eV, respectively, while the E_{VB} for TiO₂ and 6C-TiO₂ were 2.96 eV and 2.86 eV, respectively, indicating that the redox potential of the VB for both samples were sufficient to stimulate holes as electron acceptors. Bjelajac et al. [80] reported that doping of N nanoparticle to commercial P25 TiO₂ powder increased the CO₂ photoreduction activity. The average CH₄ production rate was found to be 0.191 μmol g⁻¹ h⁻¹, while the CO production rate was μmol g⁻¹ h⁻¹.

Substitutional nonmetal doping often presents defect states concentrated at the impurity location, lowering the band gap, and creating apparent absorption capacity [22]. As the degree of nonmetal doping increases, the defects rate also improves, and hence the photocatalytic activity hinders. As a result, considerable care must be taken in nonmetal doping to optimize the dopant concentration for higher visible light absorption and enhanced photocatalytic activity while maintaining an acceptable level of defects [22,81]. Co-doping using an electron donor-acceptor pair is a typical technique for reducing charge recombination in nonmetal doped TiO₂. Recently, Foghani et al. [81] used Cu/P co-doped g-C₃N₄@TiO₂ photocatalyst for improving visible light photocatalytic CO₂ reduction. The results showed that P and Cu doping increased the specific surface area, reduced the band gap energy and recombination rate while extending light adsorption to the visible region. The optimum CH₃OH production yield was recorded 859 μmol g⁻¹

h⁻¹, nearly 5 and 11.6 times greater than g-C₃N₄ and TiO₂, respectively.

3.4.4. Carbon based material doping

The synthesis of carbon-based materials with TiO₂ is an appealing approach in the field of photocatalytic activity. This is due to the availability, affordability, high specific surface area, substantial corrosion resistance, strong electrical and thermal conductivity, and controllable surface properties of carbon-based materials [82]. Most used carbon-based materials into TiO₂ catalysts are graphene, graphene oxide (GO), reduced graphene oxide (rGO), carbon nanotubes (CNTs), and carbon quantum dots (CQDs) for improving CO₂ photoreduction [83,84]. Wang et al. [20] examined porous hyper-crosslinked polymer-TiO₂-graphene composite photocatalysts for CO₂ conversion under visible light irradiation. The constructed composite structure had a large surface area of 988 m² g⁻¹ and a high CO₂ uptake capability of 12.87 wt %. This composite exhibited excellent photocatalytic activity, particularly for CH₄ generation (27.62 μmol g⁻¹ h⁻¹). Yang et al. [85] constructed TiO₂ spherical shells with modified by graphene to enhance photocatalytic activity for CO₂ reduction. This double-sided modification technique substantially enhanced the shell's contact area, allowing more photoelectrons to be separated from both sides of the shell. The main product was CO, with a little amount of CH₄ detected. Olowoyo et al. [86] synthesized reduced graphene oxide-TiO₂ composites for improving CO₂ photoreduction to CH₃OH. They found that due to the alteration in the band gap and promoting the separation of photo-generated carriers photocatalytic CO₂ reduction was improved, providing a CH₃OH generation rate of 2.33 mmol g⁻¹ h⁻¹. Fernández-Catalá et al. [87] investigated Cu_xO-doped TiO₂ photocatalyst adapted with CNTs for CO₂ photoreduction. Using low-power LED lighting, they identified a CH₄ generation rate of 117 μmol g⁻¹ h⁻¹, which was the highest values documented for any reactor design or catalytic system. The choice of an appropriate hole scavenger and successive tuning of its concentration were crucial in achieving such CH₄ production rates.

Some studies have shown that when TiO₂ nanostructured materials, particularly TiO₂ nanotubes (TNTs) and TiO₂ nanorods (TNRs), are

treated with reduced graphene oxide and carbon quantum dots, photocatalytic CO₂ conversion activity is significantly increased. For instance, Khatun et al. [88] prepared rGO modified TNTs as visible light supportive catalyst for reducing CO₂ to CH₄. TNTs with rGO inserted showed a higher rate of electron-hole separation. The increased photocatalytic activity of rGO with TNTs was confirmed by increased CO₂ to CH₄ conversion, which resulted in improved CH₄ generation (9.27%), which is 1.81-fold greater than the CH₄ generation rate obtained with TNTs (5.12%). In another study, modification of TNTs with biomass derived CQDs for enhanced CO₂ photoreduction was carried out by Zhang et al. [89]. The CO₂ photoreduction is found highest in the composite generated by combining 10 mL of CQDs solution with TNTs, yielding CO and CH₄ of 13.55 and 3.54 μmol g⁻¹ h⁻¹, respectively, which are 2.4 and 2.5-fold that of TNTs. Liu et al. [90] synthesized rod-like TiO₂ modified rGO composite for highly efficient visible-light driven CO₂ photoreduction. The produced composite had a large specific surface area of 287.3 m²/g with pore volume of 0.72 cm³/g, allowing for excellent reactant absorption and rapid intraparticle molecular transfer. CO₂ was successfully converted to methanol (MeOH), methane (CH₄), ethanol (EtOH), and dimethyl ether (DME) using the composite (Fig. 14a). The total carbon yield of G-25Ti (TiO₂-rGO with 25 mmol Ti⁴⁺) was found to be 15.7 times greater than that of pristine P25 (Fig. 14b). Carbon conversion was shown to be more than 6 times higher in P25 doped rGO composites than in pure P25. The order of CO₂ conversion, according to their findings, is G-25Ti > G-20Ti > G-15Ti, depending on the amount of rGO present.

3.4.5. Dispersion on supports

The dispersion of TiO₂ on different types of supports improves the electronic properties, product selectivity as well as pore structure of catalysts [22]. Besides, this modification strategy also overcomes the requirement for post-treatment dissociation and offers a large surface area. This approach has two key challenges: low mass transfer rate and light absorption efficacy. TiO₂ photocatalysts can be immobilized on substrates like fibers, membranes, glass, carbonaceous materials, silica, and clays through dip or spin coating [91]. Dip coating is usually recommended over spin coating because of its scale-up adaptability, improved controllability, superior structural and optical properties [22].

Tasbihi et al. [92] examined the photocatalytic performance of mesoporous silica-supported dip-coated Pt/TiO₂ for CO₂ photoreduction to CH₄. All photocatalysts had substantial carbon products of CH₄ and CO, with low quantities of CH₃OH. It has been discovered that supporting Pt/TiO₂ catalysts on mesoporous silica protects the reaction's selectivity for CH₄ production and increases the activity of Pt/TiO₂ photocatalysts. For CO₂ photoreduction to produce CH₄, Larimi et al. [93] evaluated the photocatalytic performance of carbonaceous materials supported photocatalysts coated with Pt-TiO₂. Photocatalytic performances of the synthesized photocatalysts were influenced by the particle size and carbonaceous supports applied and followed an order: multi-walled CNTs > single-walled CNTs > rGO > activated carbon. When compared to other samples, Pt-TiO₂/multi-walled carbon nanotubes had greater catalytic activity and reached a maximum yield of CH₄ (1.9 μmol g⁻¹ h⁻¹). The photocatalytic activity of glass supported NiO/TiO₂ photocatalysts was explored by Ku et al. [94] for photoreduction of gaseous CO₂ to hydrocarbon fuels. They observed that the distribution of Ni, Ti, and O atoms on the surface of these photocatalysts was consistent, and that the BET surface areas varied slightly as NiO loading increased. Meanwhile, the absorption edge of produced photocatalysts has shifted towards the visible region, lowering the bandgap energy. Methane was identified to be the main product and maximum production (4.69 mmol g⁻¹ h⁻¹) was recorded for 10 wt% NiO/TiO₂ loading which was 2-fold higher than pure TiO₂.

3.4.6. Surface sensitization

Surface sensitization is vital for increasing the efficiency of photoexcitation processes and expanding the photocatalyst's useable light

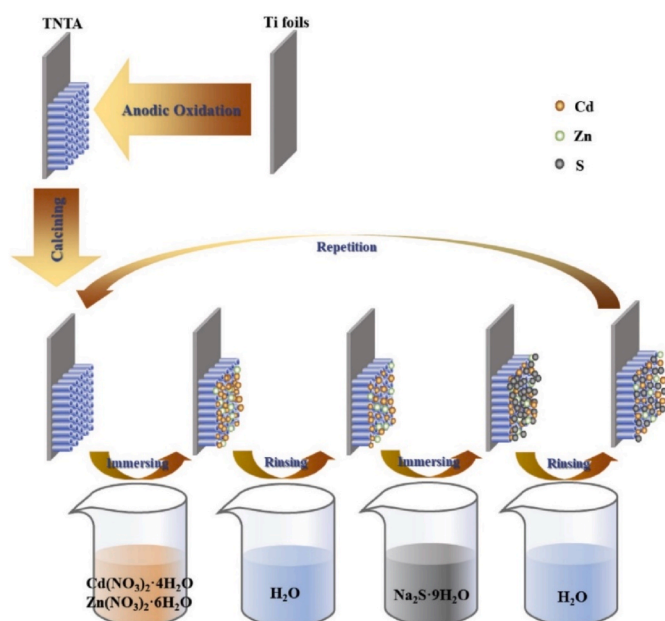


Fig. 15. Experimental illustration of surface sensitization with CdS/ZnS on TiO₂ nanotube arrays (Adopted from Ref. [97] with permission from Elsevier).

wavelength through excitation [78]. The sensitizers can improve the visible light utilization of a semiconductor photocatalysts [95]. The semiconductor is mostly used as a charge carrier instead of a generator of electrons and holes, and the process is extremely fast. Sensitizers based on dyes are one of the most extensively used sensitizers. The dye and semiconductor (TiO₂) have different roles in dye sensitization process, with TiO₂ acting as an electron acceptor and the dye acting as a light harvester. Jo et al. [96] synthesized light-sensitized squaraine (SQ) dyes and merged them into dye-sensitized catalysts (DSCs) with combination of SQ/TiO₂/Cat, and their efficacies were assessed in terms of CO₂ reduction rate. After the induction time, the photodegraded SQ was found to function as a true photosensitizer under high energy irradiation (>400 nm), yielding 16.5 μmol for 70 h.

Under visible light irradiation, Cheng et al. [97] evaluated the photocatalytic conversion performance of gas phase CO₂ by TNT arrays sensitized with CdS/ZnS quantum dots. The method of successive ionic layer adsorption (SILAR) was used to deposit CdS/ZnS composite as quantum dots (QDs) onto TNTA, as shown in Fig. 15. As the SILAR cycle number increased, the yield of principal product (methanol) enhanced and then reduced, and the performance of CdS/ZnS-TNTA was recorded 2.73 times higher than pristine TNTA. Chon et al. [98] developed an InP-QD-sensitized hybrid photocatalyst (InP-QD/TiO₂/ReP) and tested it as a low-energy photosensitizer. It was observed that the photoexcited electron transfer mechanism from the photoexcited InP-QD* to the inorganic TiO₂ solid is aided by InP quantum dot sensitization on the TiO₂ surface, leading to higher charge separation at the InP-QD/TiO₂ interface. The InP-QD-sensitized TiO₂ hybrid (InP-QD/TiO₂/ReP) displayed highly efficient and reliable photocatalytic CO₂-to-CO conversion activity in a single run under comparatively lower energy irradiation (>500 nm), with a turnover number of 2500 for 26 h.

3.4.7. Heterojunction

Heterostructures synthesis is undoubtedly the most effective approach presently being used for improving the photocatalytic performance of TiO₂ [78]. Heterostructure is developed by integrating two semiconductors that have compatible characteristics that allow the heterostructure to show better performance than the individual semiconductors [99]. The photoreaction in a heterostructure commences with photocatalytic reaction and excitation of the individual semiconductor materials that make up the heterostructure, just as it does in

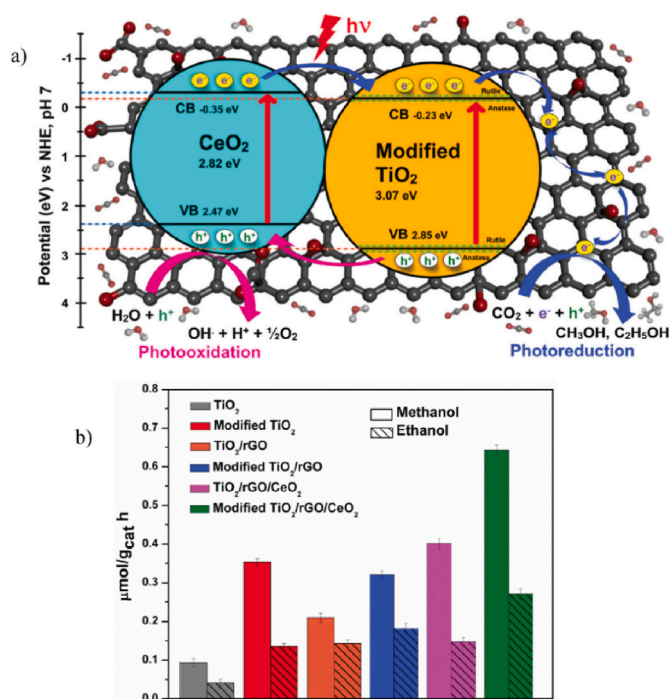


Fig. 16. Heterojunction photocatalysts for CO₂ photoreduction (a) photoreduction mechanism of modified TiO₂/rGO/CeO₂ photocatalysts and (b) CH₃OH and C₂H₅OH yields for various photocatalysts (Adopted from Ref. [100] with permission from Elsevier).

all pure photocatalysts. Seeharaj et al. [100] developed heterojunction photocatalysts by mixing surface modified titanium dioxide (TiO₂) nanoparticles with rGO and cerium oxide (CeO₂) for conversion of CO₂ to CH₃OH and C₂H₅OH. The mechanism of CO₂ photoreduction to produce CH₃OH and C₂H₅OH by utilizing TiO₂/rGO/CeO₂ composite

photocatalysts is depicted in Fig. 16a. The customized TiO₂/rGO/CeO₂ photocatalysts showed excellent photocatalytic activity by generating CH₃OH at 641 μmol g⁻¹ h⁻¹ and C₂H₅OH at 271 μmol g⁻¹ h⁻¹, almost 7-fold higher than pristine TiO₂ (Fig. 16b).

TiO₂-based heterojunction can be classified into three types for photoreduction of CO₂ considering the charge carrier separation process: typical type II, direct Z-scheme, and S-scheme heterojunction [101, 102]. Table 3 presents the summary of recent studies conducted using these types of heterojunction methods for photocatalytic CO₂ photoreduction. The most common heterojunction approach for improving TiO₂'s CO₂ reduction efficiency is type-II heterojunction. Coupling semiconductor type-A with a higher CB and semiconductor type-B with a lower VB can generate a standard type-II heterojunction photocatalyst. Wang et al. [103] found the greatest production of CH₄ among the research on type II heterojunction shown in Table 3. They evaluated the photocatalytic performance of produced g-C₃N₄/TiO₂ photocatalysts after exposing them to an 8W UV lamp for 4 h. Z-scheme type of heterojunction is comprised of two semiconductors connected by appropriate intermediate couples. The Z-scheme heterojunction is increasingly employed because to its high electron-hole separation rate, robust redox ability, and wide range of light response [104]. Recently, Kamal et al. [105] developed plasmonic Au nanoparticles that were photo-deposited on a TiO₂-coated N-doped graphene heterostructure catalyst, resulting in significantly increased CO₂ reduction activity and good selectivity for methane generation. Researchers are moving forward with the Step-scheme (S-scheme) heterojunction approach due to some drawbacks of the two methods previously described. S-scheme heterojunction is made up of staggered band reduction and oxidation photocatalysts, and it's comparable to a type-II heterojunction just with an entirely distinct charge-transfer mechanism [106]. Tahir & Tahir [107] synthesized a ternary g-C₃N₄/TiO₂/Ti₃AlC₂ S-scheme heterojunction photocatalyst to obtain the highest CH₄ yield of 2103.5 μmol g⁻¹ h⁻¹ with 96.59% selectivity.

Table 3

Summary of recent photocatalytic CO₂ reductions using various types of heterojunction modification methods.

Photocatalyst	Reductant	Reactor	Mode of heterojunction	Type of light	Product	Yield (μmol g ⁻¹ h ⁻¹)	References	
BiVO ₄ /Bi ₄ Ti ₃ O ₁₂	CO ₂ +H ₂ O vapor	Schlenk flask reactor	Type II	300W Xe lamp	CH ₃ OH	16.61	[108]	
g-C ₃ N ₄ /TiO ₂	Triethanolamine + NaOH	Photochemical reactor		8W UV lamp	CO CH ₄	13.29 72.2	[103]	
In ₂ S ₃ /TiO ₂	CO ₂ + H ₂ O	Stainless steel reactor	Z-scheme	300W Xe lamp	CO	56.2	[109]	
Pt-SrTiO ₃	CO ₂ +H ₂ O	Gas-closed circulation system		300W	CH ₄	26.7		[110]
SnS ₂ -Ti ³⁺ /TiO ₂	Dimethylformamide + H ₂ O	Pyrex reactor		Xe lamp Simulated solar light	CO	58	[111]	
ZnFe ₂ O ₄ /Ag/TiO ₂	CO ₂ +H ₂ O	Fixed bed photoreactor		200W Hg lamp	CO	1025	[112]	
CuCo ₂ S ₄ @3B-TiO ₂	CO ₂ +H ₂ O	Batch liquid-gas photoreactor		250W Hg lamp	CH ₄ CH ₃ OH CH ₄	132 30.8 42.2	[113]	
Au-NG-TiO ₂	CO ₂ + NaHCO ₃	Quartz reactor	S-scheme	300W Xe lamp	CO	25.5	[105]	
CdS/TiO ₂	CO ₂ +H ₂ O	Quartz reactor		350 W Xe lamp	CH ₄	742.4		[114]
TiO ₂ /polydopamine	CO ₂ +H ₂ O	Pyrex glass reactor		350 W Xe lamp	CH ₄	27.85 1.5		[21]
CsPbBr ₃ @ mesoporous TiO ₂	CO ₂ +H ₂ O+ C ₄ H ₈ O ₂	Sealed circulation reactor		300 W Xe lamp	CH ₃ OH CH ₄	0.26 145.28	[115]	
g-C ₃ N ₄ /TiO ₂ /Ti ₃ AlC ₂	CO ₂ +H ₂ O	Fixed bed monolith photoreactor		35 W HID car lamp	CH ₄	2103.5	[107]	

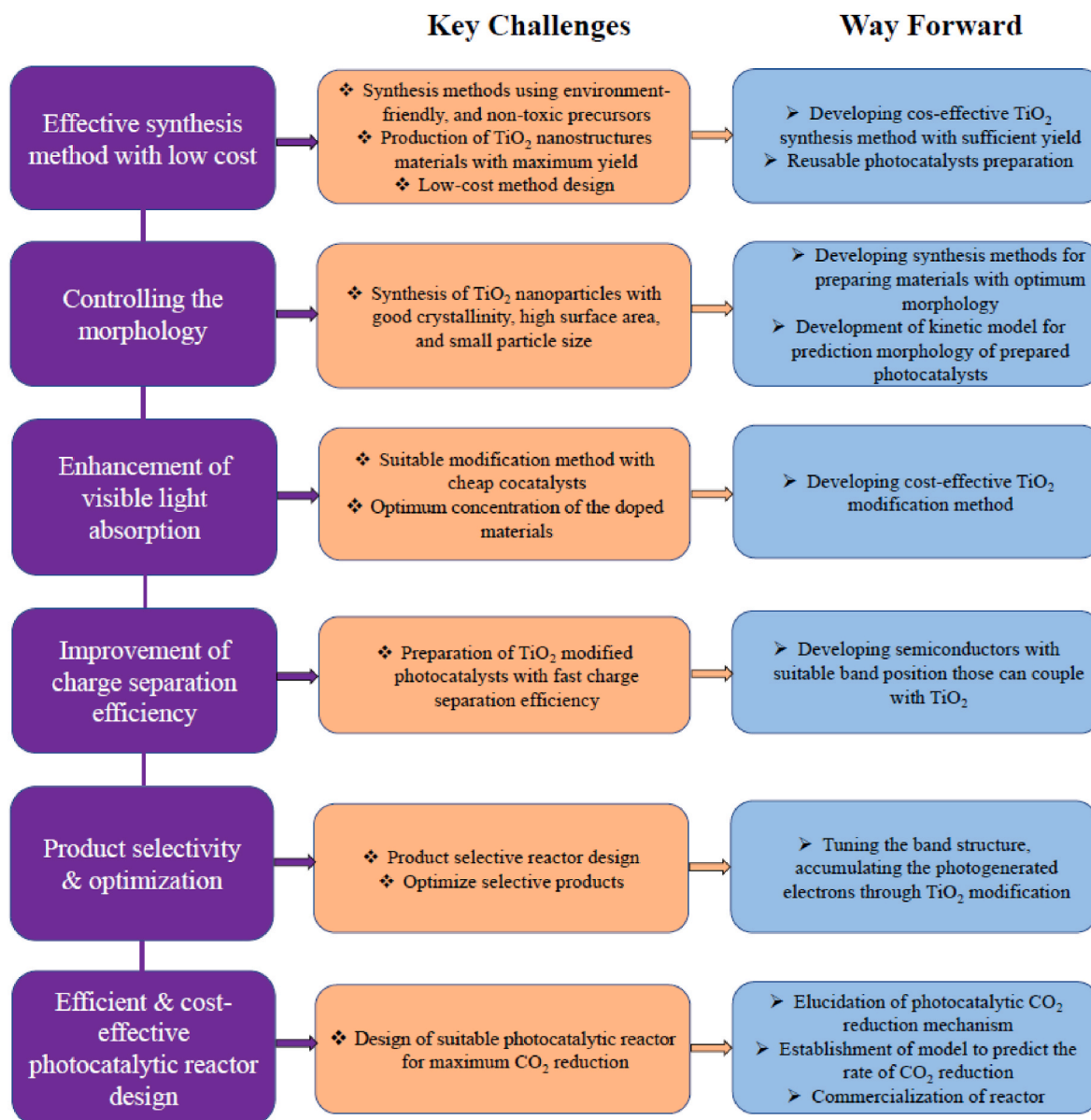


Fig. 17. Key challenges for CO₂ photoreduction to hydrocarbon fuels of TiO₂-based photocatalysts.

3.5. Challenges for photocatalytic CO₂ reduction to hydrocarbon fuels

Enormous research works are ongoing to improve the performance of TiO₂-based photocatalysts for CO₂ photoreduction. However, there are still a lot of challenges to be solved for practical application of TiO₂ as a photocatalyst to efficiently use sunlight and CO₂ for the production of hydrocarbon fuels. These are presented in Fig. 17 along with suggestions to address them and are discussed in more detail below.

- Synthesis methods are very crucial that directly influence the properties of photocatalysts as well as whole photocatalytic process. Developing cost effective synthesis method with sufficient yield of photocatalyst is a big challenge. Future research should concentrate on developing novel synthesis techniques using affordable, environmentally friendly, and non-toxic precursors for the production of reusable photocatalyst materials.
- Synthesis of TiO₂ nanostructures materials with a desired morphology such as pore size, length, and wall thickness have great influence on photocatalytic CO₂ reduction efficiency. Electrochemical anodization is a promising approach in the preparation of

TiO₂ nanoparticles since this method has the scope to tune materials with required morphology and quantity by adjusting different anodization parameters. There is a scope to work on the development of kinetic model to predict the morphology of prepared photocatalyst.

- The initial phase in photocatalysis is the absorption of light; more light absorption leads to increased electron-hole formation on the photocatalytic surface, which enhances photocatalytic CO₂ reduction. Thus, the enhancement of this process under visible light is a critical step in hydrocarbon fuels production activity. Generally different modification methods are used for improving the performance of photocatalysts under visible light irradiation. Finding the optimal percentage of the doped materials is the key issue in the surface modification process. For its broad range of practical applications, the recyclability modified photocatalysts is also vital. Even a photocatalyst with excellent photoconversion potential, will not be treated as feasible if its long-term stability is insufficient. Therefore, for practical application of TiO₂ in CO₂ photoreduction, it is indispensable to develop a suitable photocatalyst in terms of stability and efficiency through surface modification.

- The performance of TiO₂ photocatalysts for CO₂ photoreduction also depends on the charge separation process. After the excitation phase, the electron-hole must be successfully separated and moved to the photocatalyst's surface to start the redox reaction. The charge carriers will recombine if this process is not carried out as quickly as possible. Noble metals were used as a co-catalyst in the majority of published research to increase charge separation efficiency, however these metals are quite expensive. Therefore, research should be done to find appropriate cheaper and available transition metals. Additionally, composite construction between two semiconductors with appropriate band positions may also be able to enhance the performance of charge separation. However, since not all semiconductors can couple with TiO₂, finding semiconductors that fulfil the specifications may be challenging.
- It is usually recognized that photocatalytic CO₂ reduction can produce a variety of products. To optimize targeted product and for understanding CO₂ photoreduction mechanism, product selectivity has great importance. To make the subsequent separation step easier, a good selectivity of particular hydrocarbon fuel production is greatly preferred. The end product of photocatalytic CO₂ reduction is strongly influenced by both the redox potential and surface density of electron. Thus, a potential way to manage the photocatalytic CO₂ reduction's selectivity is by modifying the TiO₂ band structure. Furthermore, it is also vital to establish a rigorous, reliable, and stable system for product detection.
- Finally, away from the synthesis and modification of photocatalyst material, photocatalytic reactor design and understanding the reaction mechanism are other major areas for CO₂ photoreduction to hydrocarbon fuels. The yield of CO₂ photoreduction depends mainly on intensity of incident light and photocatalysis material and photoreactor used. However, proper photoreactor design and a deeper understanding of the reaction mechanism in photoreactor are the only ways to significantly increase the performance of photocatalytic materials. The studies of CO₂ photoreduction to date have mainly focused on the overall yield of the products. For further utilization of TiO₂ modification, detailed research on the CO₂ photoreduction mechanism on the TiO₂ surface is still lacking. On a broad scale, there is still little understanding of reaction mechanisms, reaction routes, and kinetic and thermodynamic studies of the CO₂ photoreduction process. The use of photocatalytic materials will be improved by more study in the fields of photochemistry and surface chemistry, which will result in a deeper understanding of the activities occurring at the photocatalyst's surface. This kind of strategy will provide a comprehensive and sustainable evaluation of photocatalytic CO₂ reduction to hydrocarbon fuels and its potential as a long-term strategy to address greenhouse gas emissions and energy production.

4. Conclusion

This systematic review was conducted in respect to address the recent advances in CO₂ photoreduction along with future challenges to produce hydrocarbon fuels. From 17 countries of the world 62 articles were identified for review based on the selection criteria. Recent advancements in TiO₂-based photocatalysts and the development of modification strategies for photocatalytic CO₂ reduction have been systematically examined in this review. More importantly, this review highlighted the influencing factors affect photocatalytic CO₂ reduction performance over TiO₂-based photocatalysts. However, despite of intensive research on this dream prospective area, the production rates of hydrocarbon fuels rarely exceed $\mu\text{mol g}^{-1} \text{h}^{-1}$. Even though, significant improvements have been made in terms of theoretical development, surface modification and performance of TiO₂-based CO₂ photoreduction approach, it is still long way to go for practical applications. Researchers can utilize this review to set their future goals and efforts in establishing novel methodologies while taking the challenges

into consideration.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Data availability

The authors are unable or have chosen not to specify which data has been used.

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