

Review

Photocatalytic Reduction of CO₂ by Bi-Based Semiconductor: A Review on Recent Progress

Yuming Lu ^{1,2}, Jingkai Yan ^{3,*}, Wei He ^{1,2}, He Guo ^{1,2}, Feng Liu ^{1,2}, Zhenghua Yang ^{1,2} and Wenxin Hu ^{1,*}

¹ National Key Laboratory of Baiyunobo Rare Earth Resource Researches and Comprehensive Utilization, Baotou 014030, China; yuminglu@brire.com (Y.L.); hewei@brire.com (W.H.); heguo@brire.com (H.G.); liufeng@brire.com (F.L.); yangzhenghua@brire.com (Z.Y.)

² Baotou Research Institute of Rare Earths, Baotou 014030, China

³ School of Chemistry and Chemical Engineering, Inner Mongolia University, Hohhot 010021, China

* Correspondence: yan_jk@126.com (J.Y.); wenxinhu@brire.com (W.H.)

Abstract

Photocatalytic reduction of CO₂ into valuable solar fuels represents a promising strategy to address both energy crises and carbon emissions. Bismuth-based semiconductors have emerged as attractive visible-light-driven photocatalysts due to their suitable band structures, layered architectures, and tunable morphologies. This review systematically summarizes recent advances in Bi-based photocatalysts for CO₂ photoreduction. First, the fundamental principles and key challenges of CO₂ photoreduction are outlined. Subsequently, the structural and electronic characteristics of typical Bi-based materials, including Bi₂O₃, Bi₂S₃, Bi₂MO₆ (M = W; Mo), BiVO₄, and BiOX (X = Cl; Br; I), are discussed. Emphasis is placed on design strategies to enhance photocatalytic performance, such as vacancy engineering, microstructure control, crystal facet engineering, heterojunction construction, cocatalyst loading, and their combinations. A comprehensive comparison of catalytic activities under various conditions is also provided. Finally, current limitations and future perspectives are highlighted, aiming to guide the rational design of efficient and stable Bi-based photocatalysts for CO₂ conversion.

Keywords: bismuth-based semiconductors; photocatalytic CO₂ reduction; review; structural design; visible-light photocatalysis; bandgap engineering; DFT



Academic Editors: Keiko Sasaki, Sulakshana Shenoy, Jirawat Trakulmututa, Wenan Cai and Leonid Kustov

Received: 15 January 2026

Revised: 30 January 2026

Accepted: 5 February 2026

Published: 9 February 2026

Copyright: © 2026 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the [Creative Commons Attribution \(CC BY\)](https://creativecommons.org/licenses/by/4.0/) license.

1. Introduction

Human society has developed rapidly since the Industrial Revolution, resulting in serious environmental problems, especially the excessive emission of carbon dioxide [1,2]. Capturing, storing, and converting carbon dioxide into value-added products offers a dual solution to mitigate carbon emissions and the energy crisis [3–5]. Solar energy, a clean and abundant renewable source, has the potential to meet global energy demands. Converting just 10% of the solar energy on 0.3% of the Earth's surface could surpass the energy requirements projected for 2050 [6]. Photocatalytic CO₂ reduction can utilize endless solar energy as the only energy source to directly convert CO₂ and H₂O into hydrocarbon solar fuels [7–11]. These solar fuels can be burned or used in fuel cells, which release carbon dioxide, which in turn creates a closed carbon cycle [12]. On the one hand, this approach enables high-density storage of solar energy, mainly in the form of C-H chemical bonds, solving the problem that renewable energy usually only provides an intermittent and unreliable energy supply. On the other hand, it also reverses the dilemma that CO₂ is a useless exhaust gas.

In 1972, Fujishima and Honda proposed in the journal *Nature* that titanium dioxide anodes can successfully decompose water to generate hydrogen under near-ultraviolet irradiation, which opened the prelude to semiconductor photocatalysis [13]. Six years later, Halmann first reduced CO₂ to HCOOH, CH₄, and HCHO through p-GaP single crystal under ultraviolet light irradiation [14]. Since its inception, semiconductor photocatalytic CO₂ reduction has garnered significant research interest. However, its low efficiency and poor product selectivity hinder its widespread application [15–17]. TiO₂, known for its excellent performance, low cost, and non-toxicity, remains one of the most widely used photocatalysts. Nevertheless, TiO₂'s photocatalytic activity is limited to ultraviolet light, and its performance under visible light is minimal [18–20]. Therefore, developing photocatalysts responsive to visible light is of paramount importance.

Metal oxides [21,22], such as TiO₂, are widely used in photocatalytic CO₂ reduction [23–26]. They are stable and inexpensive. However, many oxides absorb mainly UV light, and their visible-light activity is limited. Carbon-based photocatalysts and carbon nanomaterials are also studied. They provide high surface area and fast electron transport. Yet, their intrinsic active sites for CO₂ activation are often weak, and they are commonly used as supports or co-catalysts. MOF-based [27–30] and related porous systems [31,32] offer tunable pore structures and strong CO₂ uptake. Still, their long-term stability under irradiation and in the presence of water can be a concern. These limits motivate the search for visible-light-active semiconductors with stronger CO₂ activation ability. In this context, Bi-based photocatalysts are attractive. Their valence band often contains Bi 6s–O 2p hybrid states [33], which helps narrow the bandgap and extend light response to the visible region. Many Bi-based compounds also have layered structures. This feature can build an internal electric field across layers and assist charge-carrier separation and transport. In addition, vacancies and surface defects can be introduced more readily in many Bi-based lattices [34]. These sites can strengthen CO₂ adsorption and activation. Therefore, Bi-based systems provide a useful platform to link band structure design with surface adsorption chemistry in CO₂ photoreduction [35–38].

In recent years, bismuth-based catalysts have received extensive attention as efficient photocatalysts excited by visible light. For the sake of stability, research mainly focuses on compounds containing Bi³⁺. First, bismuth-based photocatalysts have unique electronic band structures and controllable morphologies [39–41]. The valence band (VB) of most bismuth-based catalysts is primarily composed of the hybridization of O 2p and Bi 6s orbitals. This hybridization results in high dispersion in the VB, narrowing the bandgap and extending light absorption into the visible range. Additionally, the distortion of the lone pairs on Bi 6s orbitals causes a pronounced overlap with O 2p orbitals, which enhances carrier mobility. Second, most bismuth-based photocatalysts have a layered structure, which essentially induces the formation of an internal electric field between the layers, thereby effectively isolating and transferring charge carriers. In addition, the region between the layers is a good active reaction site, which gives the bismuth-based photocatalysts good activity and stability. Finally, bismuth-based photocatalysts can be prepared using facile, harmless, and low-cost strategies, such as hydrothermal synthesis and wet chemical methods. Therefore, the research prospects of bismuth-based photocatalysts are promising.

In recent years, research on photocatalytic CO₂ reduction, both domestically and internationally, has included reviews on TiO₂ and related titanium materials, MOF-based catalysts, graphene, two-dimensional material catalysts, and more [42–45]. Figure 1 shows the annual number of publications (2014–2026) on bismuth-based catalysts for photocatalytic CO₂ reduction based on data retrieved from the Web of Science database in January 2026. The rising trend clearly indicates growing research interest in this field. This review

aims to provide a timely overview of recent advances in bismuth-based photocatalysts for CO₂ reduction. We begin by outlining the fundamental principles and key challenges of CO₂ photoreduction, followed by a systematic summary of the compositional structures, advantages, and limitations of the main types of bismuth-based catalysts. Then, the reported regulatory strategies for optimizing photocatalytic activity are introduced, including vacancy engineering, microstructure control, crystal facet engineering, composites, and co-strategies. For ease of understanding and evaluation, we summarize the performance of the catalysts, tabulating their activities and reaction parameters. Finally, the review presents an outlook on the future development and key challenges in this field. We hope that it will offer valuable insights to researchers working on the design and advancement of bismuth-based photocatalytic materials.

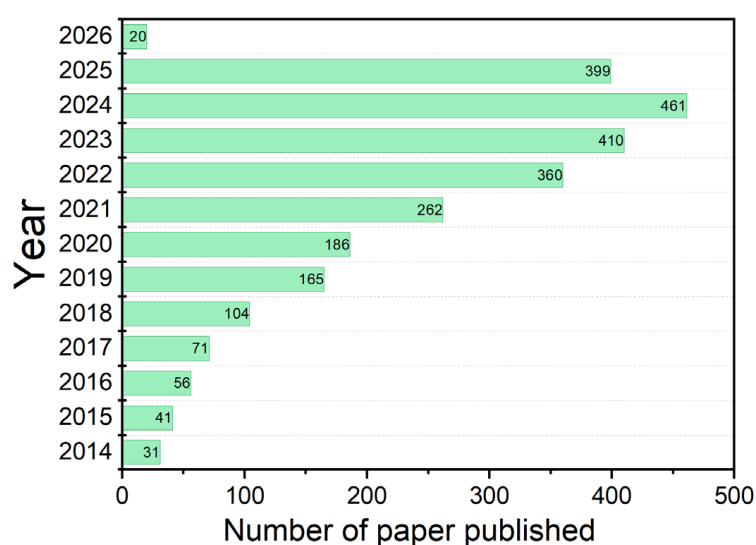


Figure 1. The annual number of published articles on bismuth-based semiconductor photocatalytic CO₂ conversion from 2014 to 2026 was obtained from the Web of Science database by searching with the theme terms “(Bi OR bismuth) AND (CO₂ OR carbon dioxide) AND (photo OR solar) AND (reduction OR conversion)” across all indexed collections.

2. Fundamentals and Challenges of CO₂ Photoreduction

CO₂ molecule exhibits a stable, linear, symmetric structure, with a C=O bond energy of 750 kJ/mol, significantly higher than that of C-H (430 kJ/mol) and C-C (336 kJ/mol), making its activation highly unfavorable [46]. Kinetically, CO₂ is non-polar and linearly symmetric, with a uniform electron cloud density around the two oxygen atoms. The carbon atom in CO₂ neither donates nor accepts electrons, contributing to the molecule's stable structure and high activation energy [47,48]. Thermodynamically, the potential required to activate CO₂ is approximately −1.44 V (NHE, pH = 0), a value that is challenging for conventional semiconductor catalysts to achieve. Furthermore, CO₂ photoreduction involves multi-electron steps and competing reactions, which slow down the overall reduction process.

As the highest oxidation state of carbon, CO₂ can be reduced to various products, such as CO, CH₄, CH₃OH, HCOOH and HCHO, by gaining different numbers of electrons and protons. In addition to these C1 products, some C2 products derived from the C-C coupling reaction, such as C₂H₄, C₂H₆, and CH₃CH₂OH, can also be detected in the photocatalytic CO₂ reduction reaction. The photocatalytic CO₂ reduction reaction is a complex multi-step reaction. In general, the photocatalytic CO₂ reduction process can be subdivided into the following steps. (i) The semiconductor is excited by a suitable light source, and then a large number of electrons and holes is generated. (ii) Photogenerated carriers are separated from

the bulk and transferred to the photocatalyst surface. (iii) CO_2 and H_2O are simultaneously captured and activated on the photocatalyst surface as reactants. (iv) Photogenerated electrons efficiently undergo catalytic reduction at the active sites on the catalyst surface, while photogenerated holes are consumed by H_2O or sacrificial reagents, producing O_2 or other oxidation products. (v) The resulting products desorb from the photocatalyst surface, re-exposing the active sites for subsequent catalytic reactions. In this section, we also briefly discuss the challenges associated with photocatalytic CO_2 conversion.

2.1. Limited Light Absorption

The solar spectrum consists of approximately 5% ultraviolet radiation, 43% visible radiation, and 52% infrared (IR) radiation, and much of the solar spectrum consists of visible and infrared regions. Therefore, generating a large number of charges by absorbing visible or infrared light is a key development trend in semiconductor photocatalysis. The ability of semiconductor photocatalysts to generate efficient photogenerated electrons and holes is a crucial starting step in photocatalysis. In the CO_2 photocatalytic reduction reaction, photoexcitation properties, energy band structure, and the separation efficiency of photogenerated carriers are three important factors that influence the behavior of photogenerated electrons in the CO_2 reduction process.

Photoexcitation properties include photon energy and light intensity. Photon energy determines whether a semiconductor can absorb photons for excitation, thermodynamically influencing product selectivity. Light intensity, on the other hand, determines the number of photogenerated electrons and holes, which kinetically affects the reaction rate and product selectivity in multi-electron reactions. Many common semiconductors have bandgaps or potentials that limit their ability to absorb sufficient sunlight to drive product formation. While wide-bandgap semiconductors are suitable for redox processes, they are only effective in the shorter wavelength region. For example, TiO_2 , with a bandgap of 3.2 eV, absorbs only in the UV region, making it inactive for visible-light-induced CO_2 conversion. Semiconductors with narrow bandgaps can absorb visible light but tend to suffer from simultaneous reduction and oxidation reactions on the surface, along with rapid recombination of holes and photogenerated electrons [49]. Cu_2O , a promising catalyst with a narrow bandgap (2.2 eV), efficiently absorbs photons in the visible range, but its narrow bandgap also causes rapid charge recombination, limiting its catalytic performance. Furthermore, photogenerated holes induce self-oxidation of Cu_2O , reducing its photostability [50]. In contrast, stable Bi-based catalysts with appropriately tuned bandgaps offer promising potential for CO_2 conversion.

2.2. Adsorption of CO_2

The adsorption of CO_2 on the semiconductor surface is a key first step in the CO_2 photoreduction reaction. The adsorption interaction results in a partially charged species, $\text{CO}_2^{\delta-}$. As shown in Figure 2, the main adsorption modes of CO_2 on the semiconductor surface include oxygen coordination, carbon coordination, and mixed coordination [51,52]. Figure 2a,b,c show two possible bidentate binding structures in oxygen coordination, forming a typical carbon coordination for a carbonate-like species and mixed coordination, respectively [53]. Different binding modes determine the different $\text{CO}_2^{\delta-}$ reaction pathways to a certain extent. In Figure 2, solid lines represent the intrinsic covalent $\text{C}=\text{O}$ bonds within the CO_2 molecule, while dashed lines indicate the adsorption interactions between CO_2 and the surface active sites of catalysts, such as Lewis acid–base interactions or coordination bonds. The light green and dark green spheres denote surface Lewis acid sites and Lewis base sites, respectively.

Poor CO₂ adsorption will reduce the amount of CO₂ available for reduction. Therefore, enhanced CO₂ adsorption on the semiconductor surface can significantly improve the CO₂ reduction efficiency. Functionalization of the catalyst surface with hydroxyl (OH), amino (NH₂) groups, or oxygen vacancies may donate electrons to CO₂ molecules, resulting in negatively charged HCO₂^{δ−} species that can increase CO₂ adsorption [54]. The use of semiconductors with a large surface area can also provide more active sites for the catalytic reaction while improving the CO₂ adsorption capacity [55]. In addition, the alkali metal or alkaline earth-metal-loaded semiconductor has a great affinity for acidic CO₂ molecules, which can also promote the adsorption of CO₂ on the catalyst surface [56].

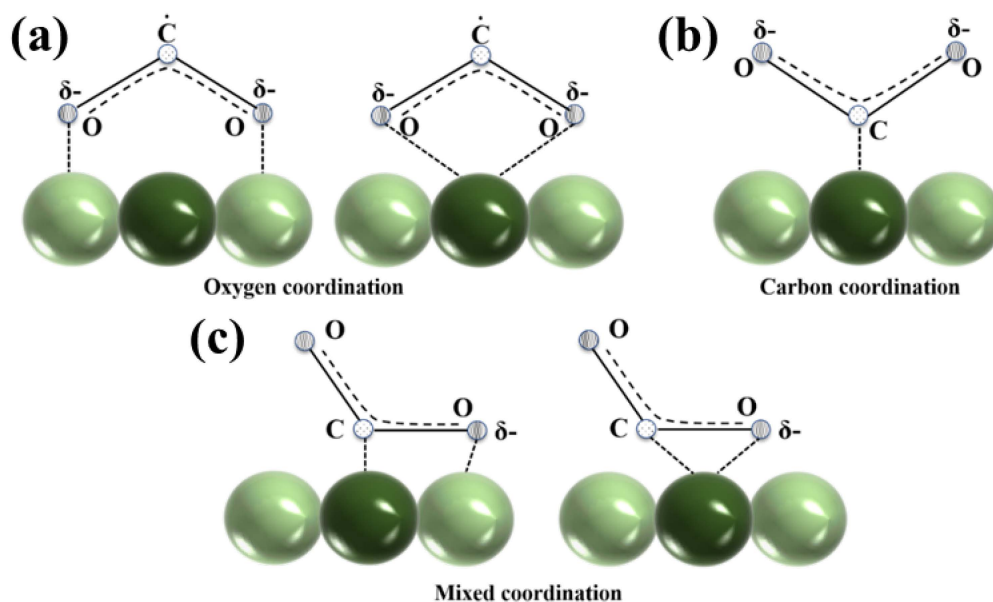


Figure 2. The possible structures of CO₂ activation to CO₂^{δ−} on catalysts. (a) Single coordination of CO₂ through O atoms with surface Lewis acid sites; (b) Single coordination of CO₂ through the C atom with surface Lewis base sites; (c) Mixed coordination mode involving simultaneous interactions of C atoms with Lewis base sites and O atoms with Lewis acid sites.

2.3. Reaction Pathways

Understanding the mechanisms of CO₂ photoreduction to various products is challenging due to many known and unknown phenomena. Various factors, such as the properties of the semiconductor itself, photoexcitation properties, surface defect sites, CO₂ adsorption properties, the number of active sites, and the properties of the interface, can significantly affect the reaction pathway. These include the number of photogenerated electrons, the electron transfer rate, the electron–hole recombination rate, C–O bond cleavage, the form of the intermediate substance, the proton source, coupling of the intermediate and the proton, new bond formation, adsorption and desorption of intermediate products, etc. all play crucial roles in determining the reaction efficiency and affect the CO₂ reduction pathway [57,58]. As shown in Figure 3, three reaction pathways for photocatalytic reduction of CO₂, (a) the carbene pathway, (b) the formaldehyde (HCHO) pathway, and (c) the glyoxal (HOCCOH) pathway, are presented. All of these pathways start with the adsorption and activation of CO₂ molecules on the catalyst surface.

In Figure 3a, the green arrows clearly show the carbene pathway for the photocatalytic reduction of CO₂ to CH₄ [10,52,59]. In the carbene pathway, the process of CO₂ conversion to CH₄ can be summarized as first deoxygenation followed by hydrogenation. The carbene pathway has two important features. CO is a key intermediate or by-product, depending on its binding mode and adsorption strength on the photocatalyst surface. Furthermore, the final product is either CH₃OH or CH₄, and these are competing reactions. *CH₃OH is formed when *CH₃ recombines with hydroxyl radicals (·OH), while CH₄ is formed when *CH₃ reacts with H·. When the CO₂ molecule captures a photogenerated electron and H⁺, it forms a monodentate carbon-coordinated carboxyl group (·COOH) on the catalyst surface. This group then gains another pair of electrons and H⁺, undergoing dehydration to form CO*. If the binding energy of CO* to the semiconductor is weak, it desorbs as CO, a by-product. However, if the binding is stronger, CO* further reacts with another pair of electrons and H⁺ to form COH*. After hydrogenation and dehydration, the intermediate ·C is generated. Continuous hydrogenation steps then produce the critical intermediate ·CH₃, which combines with ·OH or H⁺ to form CH₃OH and CH₄. ·CH₃ is a key intermediate in the photocatalytic CO₂ reduction. The carbene pathway, a common mechanism for producing CO and other hydrocarbons, is supported by experimental evidence and can be monitored using advanced analytical techniques, such as EPR (Electron Paramagnetic Resonance).

In the formaldehyde pathway, CO₂ has many possible intermediate products in the photocatalytic reduction of CH₄ [60]. The yellow arrows in the middle of Figure 3b point out the possible occurrence of carbon dioxide in this process to give two, four, six, and eight electron products as HCOOH, H₂CO, CH₃OH, and CH₄, respectively. In this pathway, the photoconversion of HCOOH to H₂CO has the most significant kinetic obstacle. The formaldehyde pathway has two important features. One feature is that the combination of CO₂ and the catalyst is carried out through the combination of an oxygen atom and the active site of the catalyst. In addition, H₂CO and CH₃OH are two intermediates in the reaction process, not by-products. The distinction between intermediates and by-products depends on the surface binding of H₂CO and CH₃OH to the catalyst. If the binding mode is stronger, the release of H₂CO and CH₃OH is more difficult, which ensures that the intermediates will further undergo hydrodeoxygenation to form CH₄. On the contrary, the weak binding of H₂CO and CH₃OH on the catalyst surface leads to the direct desorption of H₂CO and CH₃OH during the reaction. Furthermore, H₂CO and CH₃OH are obvious by-products in the reaction, while CH₄ is in low or no yield. This pathway can explain the production of HCOOH, H₂CO, CH₃OH, and CH₄ but not CO.

The blue arrow in Figure 3c illustrates the reaction route of the glyoxal pathway, which is unique for involving the dimerization of formyl (HCO) radicals. This reaction generates glyoxal, an intermediate with high electron affinity, which is easily reduced to trans-ethan-1,2-semidione. This intermediate is further reduced to form ·CH₃, which then reacts with protons to produce CH₄, with CO released as a by-product [61].

Although various studies have explored these CO₂ reduction pathways theoretically and experimentally, the multiple steps involved in the reaction, the adsorption and desorption of intermediates, and the appearance of by-products make the process more complex in terms of product selectivity. During the reaction process, not only is there a competitive reaction between H₂O reduction and CO₂ reduction but also the CO₂ reduction products of different reaction pathways.

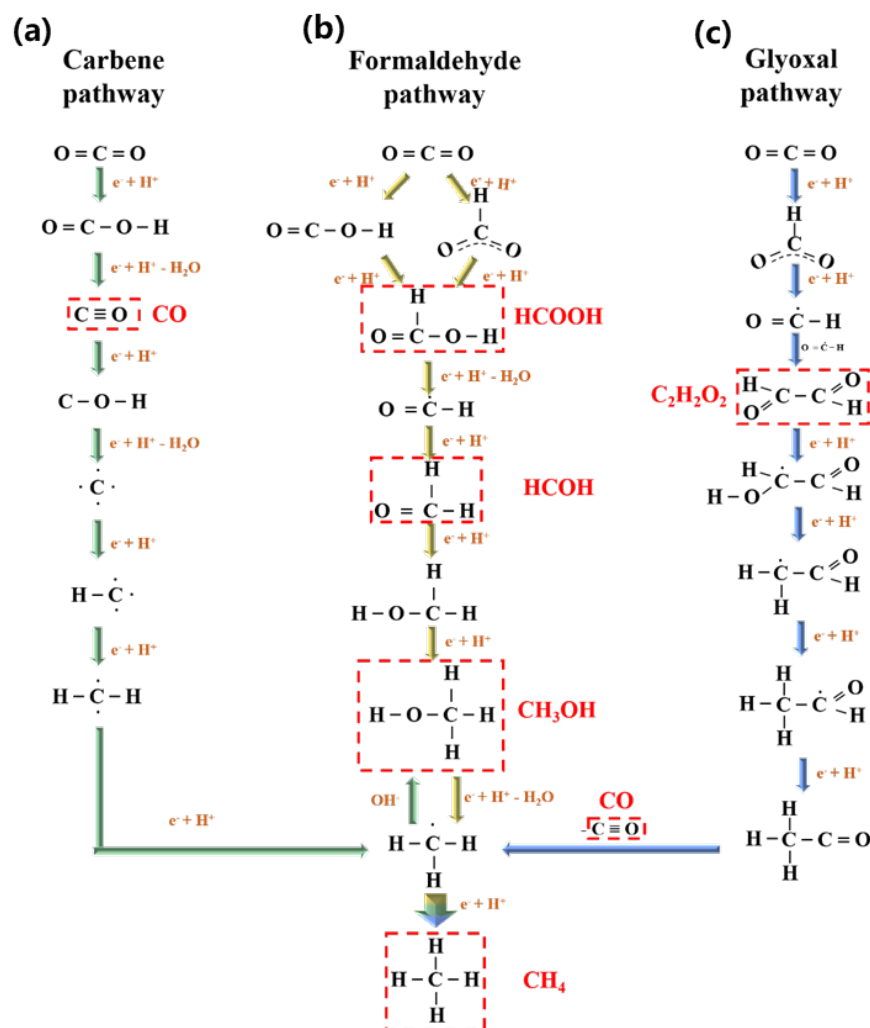


Figure 3. The possible pathways of photocatalytic CO₂ reduction to CH₄ on the surface of photocatalysts. (a) Carbene pathway; (b) Formaldehyde pathway; (c) Glyoxal pathway. Adapted with permission from Ref. [62]. Copyright 2024, Elsevier Ltd.

3. Bi-Based Photocatalysts

Bismuth (Bi), located in group VA of the sixth period in the periodic table, has an atomic number of 83 and an atomic weight of 208.98. It exhibits both covalent and metallic bonding characteristics. Most Bi-based materials used in photocatalysis possess a unique layered structure, where strong chemical interactions hold the layers together while weak van der Waals forces exist between them. These structural features contribute to the distinct physical and chemical properties of Bi-based photocatalysts. Considering the stability of Bi^{3+} , most studies have focused on compounds containing Bi^{3+} , such as Bi_2O_3 [63–65], BiVO_4 [66–68], $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [69,70], $\text{Bi}_{12}\text{TiO}_{20}$ [71], $\text{Bi}_2\text{O}_2\text{CO}_3$ [72–74], Bi_2WO_6 [68,75], BiPO_4 [76], BiFeO_3 [77], BiOX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) [78–80], $\text{Bi}_3\text{TiNbO}_9$ [81], and $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ [82]. Due to the instability of Bi^{5+} , although its compounds can be excited by visible light, there is little research on these compounds.

Compared with conventional metal oxide photocatalysts [28], such as TiO_2 [24], the valence band (VB) of Bi-based oxides contains not only O 2p orbitals but also Bi 6s orbitals. The Bi 6s orbitals contribute to reducing the bandgap and enhancing the mobility of photogenerated charges in semiconductors. As a result, Bi-based photocatalysts typically have a bandgap of less than 3.0 eV, allowing them to be excited by visible light, as shown in Figure 4. The crystal structure and electronic properties play a significant

role in photocatalytic activity. This section discusses the crystal and electronic structures of several well-known Bi-based photocatalysts and evaluates their performance in photocatalytic reactions.

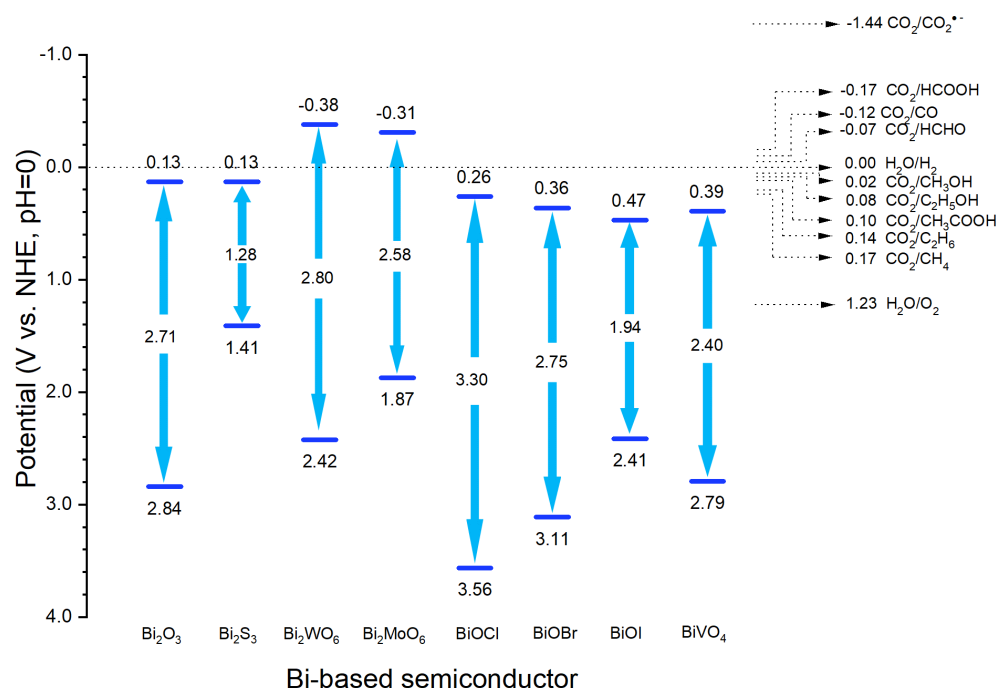


Figure 4. Energy diagram of Bi-based photocatalysts and redox potentials versus NHE of CO₂ reduction and water splitting at pH = 0.

3.1. Bi₂O₃ and Bi₂S₃

Bi₂O₃ (Bismuth (III) Oxide) as an important oxide of the Bi element in nature. Bi₂O₃ is a light-yellow powder with a melting point of 824 °C and a boiling point of 1890 °C. It is soluble in acid but insoluble in water and alkali. The density of Bi₂O₃ varies slightly with different crystal types, ranging from 8.2 g·cm⁻³ to 8.9 g·cm⁻³.

Bi₂O₃ is a p-type semiconductor, with several crystal forms resulting from the symmetry of the unit cell, including monoclinic (α), tetragonal (β), body-centered cubic (γ), face-centered cubic (δ), orthorhombic (ϵ), triclinic (ω), and hexagonal structures [83,84]. Of these phases, only the α -Bi₂O₃ and γ -Bi₂O₃ phases exhibit semiconductor properties, while the β -Bi₂O₃ and δ -Bi₂O₃ phases behave as oxide ionic conductors. Furthermore, α -Bi₂O₃ is stable at low temperatures, δ -Bi₂O₃ is stable at high temperatures, and the other crystal phases are metastable phases, and there is a conversion relationship between the four phases [63]. Although different Bi₂O₃ crystal forms all have different band positions and properties, this is generally considered a disadvantage. (i) It is difficult to synthesize well-defined Bi₂O₃ crystal phases at room temperature, usually requiring complex equipment. (ii) The phase transition of Bi₂O₃ is difficult to control and limits its practical application. In CO₂-containing solutions, metastable Bi₂O₃ will be converted to α -Bi₂O₃ and bismuth subcarbonate (Bi₂O₂CO₃). (iii) Low-temperature synthesis will lead to poor crystallization of Bi₂O₃, a crystalline phase, and, if the crystallinity is increased through high-temperature annealing, Bi₂O₃ will undergo phase transformation. But, Bi₂O₃ has obvious advantages in photocatalytic reactions. It is inexpensive, non-toxic, abundant in the crust, and inert towards neutral water. In addition, it has a suitable valence band for photocatalytic reactions, chemical and biological inertness, photo corrosion stability, and good solar light absorption. And, β -Bi₂O₃ has a unique structure, which can provide a charge transfer channel and prevent photogenerated carriers from recombining with

holes during the photocatalytic process, and it has better photocatalytic performance than other crystalline phases [85]. However, because the existence of β - Bi_2O_3 is not stable, the development and preparation of β - Bi_2O_3 is still a challenge.

Bi_2S_3 (Bismuth (III) sulfide) belongs to the A_2B_3 ($\text{A} = \text{Sb, Bi, As}$; $\text{B} = \text{S, Se, Te}$) type direct bandgap layered semiconducting material, and its crystal system belongs to the orthorhombic system. It is widely used in thermoelectric devices, photocatalysis, and infrared spectrometers [86]. Compared to Bi_2O_3 , Bi_2S_3 has a narrower bandgap (1.3–1.7 eV), which allows it to generate photogenerated carriers under visible and near-infrared light [87]. However, this narrow bandgap also leads to a higher recombination rate of photoinduced electron–hole pairs, limiting the use of pure Bi_2S_3 in photocatalysis [88]. Numerous studies have demonstrated that combining Bi_2S_3 with other materials enhances the separation and migration of electron–hole pairs, thereby improving the photocatalytic activity of bismuth sulfide [89–92].

3.2. Bi_2MO_6 ($\text{M} = \text{W, Mo}$)

Bi_2MO_6 ($\text{M} = \text{Mo, W}$) has two different crystal phases: orthorhombic and monoclinic structures. The orthorhombic crystal structure Bi_2MO_6 ($\text{M} = \text{Mo, W}$) exists in the mid-to-low-temperature range ($T < 960^\circ\text{C}$), and the monoclinic Bi_2MO_6 ($\text{M} = \text{Mo, W}$) exists in the high-temperature range ($T > 960^\circ\text{C}$). The current research in the field of Bi_2MO_6 ($\text{M} = \text{Mo, W}$) mainly focuses on the former one [93]. Bi_2MO_6 ($\text{M} = \text{Mo, W}$) is composed of MO_6 ($\text{M} = \text{Mo, W}$) octahedral layers and $[\text{Bi}_2\text{O}_2]^{2+}$ layers alternately stacked, presenting an aurivillius type of oxide family. Specifically, each Bi atom in Bi_2MO_6 is coordinated with six O atoms and four M atoms [94,95], while each M atom is coordinated with six O atoms, forming a co-angular octahedron [96]. Notably, the crystal directions of Bi_2MoO_6 and Bi_2WO_6 differ, with the directions perpendicular to the upward orientation of their layered structures being (010) and (001), respectively. Additionally, the local environment around each M and Bi atom in the Bi_2MO_6 unit cell is slightly distorted [97].

Bi_2MoO_6 and Bi_2WO_6 are direct-gap semiconductors. The VB of Bi_2MO_6 ($\text{M} = \text{Mo, W}$) is mainly composed of the 6s orbital of Bi and the 2p orbital of O. The CB is mainly composed of the *nd* orbital of M ($\text{Mo } 4d, \text{ W } 5d$); photo-generated electrons transition from the hybrid orbital to the *nd* orbital in photocatalytic reactions [98]. Combining the above electronic structure and layered structure of Bi_2MO_6 , it can be inferred that in the photocatalytic reaction, M is the reduction reaction site and the O in Bi-M-O or Bi is the oxidation reaction site [97,99,100].

Although the energy band structure of Bi_2MoO_6 and Bi_2WO_6 is similar, and both can absorb part of visible light, the bandgap and E_g of the two are different. It is generally believed that the E_g of Bi_2MoO_6 is about 2.6 eV and the E_g of Bi_2WO_6 is about 2.8 eV, which is slightly larger and also consistent with the yellow and light green colors of the two. In terms of energy band position, the VB position of Bi_2WO_6 is more oxidative compared to that of Bi_2MoO_6 . In addition, in order to compare the carrier separation and transport performance of Bi_2MoO_6 and Bi_2WO_6 , Lai compared the effective electronic mass of the two through density functional theory (DFT) [101]. For photocatalysts, the effective mass of electrons is inversely proportional to the curvature of the bottom of its conduction band. The calculation results show that the curvature of the conduction band bottom of Bi_2WO_6 is greater than Bi_2MoO_6 , which indicates that the effective electron mass of Bi_2WO_6 is smaller and the carrier separation and transmission efficiency are higher [102,103]. Bi^{3+} has a relatively positive reduction potential and is easily reduced to elemental Bi. As a result, Bi_2MO_6 ($\text{M} = \text{Mo, W}$) effectively degrades pollutants and converts energy, but it cannot directly cleave H_2O to produce H_2 [104]. However, Bi_2MO_6 faces several challenges as a photocatalyst: (i) its bandgap is about 2.8 eV, which enables it to absorb visible

light, but it exhibits minimal photocatalytic activity under light irradiation greater than 470 nm [105]; (ii) the recombination rate of photogenerated electrons and holes is high; and (iii) insufficient exposure of reactive sites limits the adsorption and activation of reactants.

At present, the application of Bi_2MO_6 ($M = \text{Mo}, \text{W}$) in the energy field mainly includes CO_2 reduction, nitrogen fixation reaction, oxygen production, and so on. The basic principle of these reactions is to use the redox reaction between photogenerated carriers (mainly photogenerated electrons) and substrate molecules (CO_2 , N_2 , H_2O) to realize the development and utilization of new energy [106–108].

3.3. BiVO_4

BiVO_4 (Bismuth vanadate), a narrow bandgap semiconductor, is one of the most promising photocatalysts for visible light response, drawing significant attention from researchers. BiVO_4 exists in three main crystalline forms: tetragonal scheelite (t- BiVO_4), monoclinic scheelite (m- BiVO_4), and tetragonal zircon (t-z- BiVO_4). t-z- BiVO_4 can irreversibly transform into m- BiVO_4 when heated to temperatures between 670 K and 770 K, while s- BiVO_4 and m- BiVO_4 can interconvert at 528 K [109]. Among these phases, m- BiVO_4 , with a bandgap of 2.4 eV, exhibits the highest photocatalytic performance under visible light irradiation.

The unit cell of m- BiVO_4 contains four Bi atoms, four V atoms, and sixteen O atoms. The basic structural unit consists of VO_4 tetrahedra and BiO_8 dodecahedra. Each Bi atom is surrounded by eight O atoms, forming a BiO_8 dodecahedron. Adjacent metal atoms are linked to form a continuous Z-shaped structure on the (221) face, with the BiO_8 chains parallel to the (110) face by sharing an edge. The VO_4 tetrahedra remain independent and do not touch each other. They are connected to BiO_8 dodecahedra through O atoms that share vertices. As a result, each BiO_8 dodecahedron is surrounded by eight isolated VO_4 tetrahedra. Additionally, Bi and V atoms are alternately arranged along the crystal axis, giving m- BiVO_4 its layered structure. However, the arrangement of Bi and V is different along the three different axis directions. In the a-axis or c-axis direction, it has a -Bi-V- structure; in the b-axis direction, it has a -Bi-V-V-Bi- structure. Moreover, the Bi-O bond length in the b-axis direction is longer than in the a-axis or c-axis direction, which leads to a rather weak bond. This may be the reason for the easy cracking along the (010) face. Zhao reported that there are four types of Bi-O bonds and two types of V-O bonds in m- BiVO_4 , which means that the VO_4 tetrahedron and BiO_8 dodecahedron will be slightly distorted [110]. The twisted BiO_8 dodecahedron will enhance the influence of Bi 6s on the electrons. At the same time, the distortion of the VO_4 tetrahedron causes the positive and negative charge centers to shift, creating a built-in electric field that facilitates the separation of photogenerated electron-hole pairs, thus enhancing photocatalytic activity. In contrast, the other BiVO_4 structures (t- BiVO_4 and t-z- BiVO_4) exhibit negligible photocatalytic activity under visible light, primarily due to their symmetrical polyhedral structures. This is why m- BiVO_4 shows superior visible light catalytic performance among the three structures.

Density functional theory (DFT) calculations reveal that the valence band (VB) of m- BiVO_4 is primarily composed of O 2p orbitals. The top of the VB is mainly contributed by O 2p π nonbonding orbitals, with a small contribution from Bi 6s. The center of the VB results from the hybridization of V 3d and O sp² orbitals, while the bottom is influenced by Bi 6p and hybridized O sp² orbitals. The valence band in the range of −10 to −9 eV is mainly composed of Bi 6s, hybridized with a small amount of O 2p. The conduction band (CB) is primarily composed of the hybridization of V 3d, O 2p, and Bi 6p. Below 4.8 eV, the CB is mainly composed of V 3d and O 2p, with Bi 6p contributing less. Between 4.8 eV and 7.1 eV, the contribution of Bi 6p to the CB is significantly enhanced, while V 3d's contribution is reduced. This electronic configuration not only narrows the bandgap

(Eg) of the photocatalyst, extending its visible light response, but also increases the VB width, promoting the migration of photogenerated holes and inhibiting the recombination of electron–hole pairs [110].

The actual photoelectric conversion efficiency of BiVO₄ photocatalytic material is still far lower than its theoretical value due to its own problems, which limits its practical application. The existing problems are mainly reflected in the following aspects. (i) The charge transfer in the BiVO₄ is very slow, causing about 60–80% of the charge carriers generated to recombine before reaching the surface of the material. It leads to shortcomings of the photogenerated electron–hole pairs in BiVO₄ that are difficult to separate and easy to recombine. (ii) Compared with the oxidation reaction of sulfite, the kinetic rate of BiVO₄ release of oxygen is very slow. (iii) The conduction band edge of BiVO₄ is located below the potential of the reversible hydrogen electrode, which causes its photoelectrochemical reaction to require an external bias.

3.4. BiOX (X = Cl, Br, I)

BiOX (X = Cl, Br, I) belongs to the tetragonal matlockite structure (PbFCl type) and is a compound with a ternary structure (V-VI-VII), which has a unique layered crystal structure. BiOX is mainly composed of [Bi₂O₂]²⁺ and double X[−]. Two atomic layers are alternately arranged along the C axis to form a layered structure [111–113]. The atoms in the layers are mainly connected by relatively strong covalent bonds, and the atoms between the layers are mainly connected by weak Van der Waals force. In this way, the internal non-bonding force and the external bonding force will interact to make the BiOX shows a high degree of anisotropy [114,115]. The layered crystal structure of BiOX is relatively open, providing a large enough space for the polarization of related atoms and orbitals to easily form a built-in electric field perpendicular to the [Bi₂O₂]²⁺ and double X[−]. The built-in electric field can prolong the lifetime of photoinduced charge carriers and facilitate the separation of photo-generated electron–hole pairs, improving the photocatalytic performance of the material [87,116–118].

In addition, density functional theory (DFT) calculations show that the top of the VB of BiOX is mainly composed of the hybridization of O 2p orbitals and X *np* orbitals (where the values of *n* corresponding to Cl, Br, and I are three, four, and five, respectively) and the minimum value of the CB is mainly composed of Bi 6p orbitals [78,119]. Therefore, when the *n* value of X continues to increase, the density peak of the X *np* orbital will migrate in the direction of the top of the VB, which will increase the position of the VB top of the BiOX and cause the Eg of the BiOX material to gradually decrease [36,120,121]. It is for this reason that BiOCl has the largest bandgap and only responds to ultraviolet light; BiOI has the smallest bandgap and can respond to visible light.

Building on the discussion of the hybridization of O 2p and X *np* orbitals in BiOX, further analysis of the bandgap energies reveals how the halogen ion affects the photocatalytic properties. BiOCl [122], with a bandgap of around 3.4 eV, absorbs mostly in the ultraviolet range, limiting its photocatalytic activity under visible light. The larger bandgap of BiOCl is due to the more significant overlap between O 2p and Cl 3p orbitals, which results in a higher energy level for the top of the valence band (VB) and restricts the absorption of visible light. In contrast, BiOBr [123] and BiOI [124] exhibit smaller bandgaps of approximately 2.8 eV and 1.8 eV, respectively. As the atomic number of the halogen increases from Cl to I, the X *np* orbitals' energy levels shift closer to the top of the VB, thus reducing the overall bandgap. This shift allows BiOBr and BiOI to absorb light in the visible region, making them more efficient for photocatalytic CO₂ reduction under visible light [125–127]. The relationship between halogen substitution and the narrowing of the bandgap demonstrates a strategy for optimizing BiOX materials for visible light-driven photocatalysis.

Furthermore, the defect engineering and vacancy formation in BiOX materials can further tune their electronic structure. For instance, vacancy engineering in BiOBr and BiOI enhances their photocatalytic performance by improving charge carrier separation and increasing the surface reactivity for CO₂ activation. The presence of halogen vacancies also plays a crucial role in facilitating the transfer of charge carriers, further optimizing the photocatalytic efficiency.

BiOX material is a photocatalyst to be developed due to its special layered structure and good non-toxic, anti-corrosion, and other physicochemical properties. But, its existing problems should not be underestimated: (i) a low surface area, limited light absorption, and few photocatalytic active sites make it difficult for the photocatalytic reaction to occur, and (ii) electrons and holes are not easily separated and photogenerated carriers have a very short lifetime, which in turn affects the photocatalytic activity.

4. Structural Design of Bi-Based Photocatalysts

4.1. Vacancy Engineered

Because the VB and CB edges of most Bi-based semiconductors are mainly composed of sp hybridized Bi and O orbitals, the loss of Bi or O atoms will seriously affect the properties of bismuth-based photocatalysts. Therefore, introducing vacancies is an effective method to modify the electronic structure of photocatalysts. The local polarization field created by vacancies can reduce the energy barrier, facilitating CO₂ activation by promoting electron transfer and also triggering C-C coupling by altering the asymmetric charge distribution on the intermediate [52,128,129]. Specifically, the (C-O) π^* orbitals of CO₂ accept electrons from defect sites, causing the energy level of the $2\pi_u$ orbital to decrease and the linear structure to bend. This facilitates the activation of CO₂ as a reaction intermediate, promoting further reactions. Moreover, uniform charge density on the photocatalyst surface leads to similar charge distributions in reaction intermediates, resulting in strong dipole-dipole repulsion that limits C-C coupling. However, vacancies create variations in charge density between adjacent atoms, providing electrons that enhance CO₂ activation, leading to asymmetric charge distribution in the intermediates, which promotes C-C coupling and favors the formation of the desired product.

The methods for synthesizing vacancy can be classified into “top-down” and “bottom-up” categories according to the generation sequence of the vacancy [130]. Most of the “top-down” synthesis methods involve post-processing of the original material, that is, the treatment of bismuth-based materials through methods such as heat treatment, ultrasound, light irradiation, or chemical reduction. The vacancy is created through weak out-of-plane interactions between the outer elements. One-step synthesis methods, in which vacancy defects are generated along with crystal growth through one-step hydrothermal, ionic liquid, and other methods in the synthesis stage, are classified as “bottom-up” methods. This method can simultaneously create vacancy defects in the bulk and the surface of the material and the separation of holes and carriers is further improved.

Oxygen vacancies (OVs) play a crucial role in hole engineering and significantly enhance photocatalytic performance. The CO₂ photoreduction mechanism mediated by OVs proceeds as follows. First, O atoms in CO₂ are adsorbed onto OVs and converted into lattice oxygen during the photoreduction process [131]. The intercalation of oxygen with high electronegativity into the lattice induces charge transfer at Bi-O bonds [132]. As a result, adjacent lattice oxygen with lower charge density is readily oxidized into OVs by two photogenerated holes ($2h^+$) [133]. Under illumination, this process generates new OVs with two positive charges. The O atoms from H₂O molecules then fill the OVs, generating two hydrogen protons. After the catalyst acquires electrons and hydrogen protons, different gas molecules are produced through various equilibrium states, and the catalyst returns

to its initial state. It has been reported that the formation of the $[\text{COOH}]^\cdot$ group is the rate-limiting step in CO_2 reduction to CO or CH_4 due to the high formation energy of $[\text{COOH}]^\cdot$. DFT calculations show that OV on the defect surface serve as active sites, greatly reducing the barrier for $[\text{COOH}]^\cdot$ formation.

Zhang successfully introduced oxygen vacancies into BiOCl nanoplates using light irradiation [133]. When BiOCl is irradiated under a 500 W xenon lamp for 5 h, the initially white BiOCl transforms into a gray defective form. Due to the high oxygen atom density and low Bi-O bond energy, oxygen vacancies can be easily regenerated under light irradiation, even after being filled by oxygen atoms during the photocatalytic reaction. This enables the generation and recovery of BiOCl defects (Figure 5). In another study, Bi designed $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ ultrafine nanotubes enriched with oxygen vacancies through structural deformation to enhance carrier migration and CO_2 activation [134]. Without cocatalysts and sacrificial reagents, the CO release rate from $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$ nanotubes was found to be 16.8 times higher than that from pristine $\text{Bi}_{12}\text{O}_{17}\text{Cl}_2$.

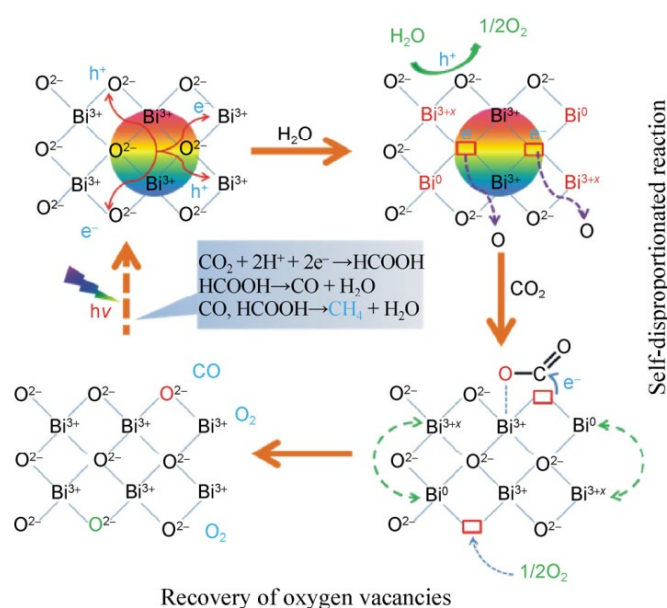


Figure 5. Possible reaction pathways for the formation of CO , CH_4 , and O_2 from CO_2 photoreduction with H_2O on BiOCl nanoplates [133]. Reprinted with permission from Ref. [133]. Copyright 2014, Springer Nature Ltd.

To investigate the impact of oxygen vacancies on photogenerated carrier separation and CO_2 activation, Wang synthesized PbBiO_2Br atomic layer photocatalysts with tunable oxygen vacancy concentrations [135]. Ultrafast transient absorption spectroscopy and DFT calculations show that photogenerated electrons migrate to the conduction band (CB) and are trapped by surface oxygen vacancies, effectively separating the electron–hole pairs. CO_2 molecules adsorbed on oxygen vacancies directly interact with surface protons to form COOH^* intermediates, which are further protonated to produce CO . During the photocatalytic reduction of CO_2 to CO , oxygen-rich vacancies serve as both electron separation and transfer centers and CO_2 adsorption sites. The PbBiO_2Br atomic layer photocatalyst with oxygen vacancies exhibits a CO release rate of $4.58 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ in water, which is 10.9 times higher than that of bulk PbBiO_2Br . Guo successfully prepared $\text{Bi}_2\text{Sn}_2\text{O}_7$ NPs with abundant ultra-small oxygen vacancies via the PVP-assisted hydrothermal method [136]. The oxygen vacancies significantly promote CO_2 activation, stabilize COOH^* intermediates, and accelerate CO desorption. Additionally, the ultra-small oxygen vacancies enhance the rate of bulk charge diffusion. These factors combined led to an 8.1-fold improvement

in the photocatalytic performance of $\text{Bi}_2\text{Sn}_2\text{O}_7$ NPs for CO_2 to CO conversion, with the CO formation rate reaching $14.88 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$. Kong synthesized Bi_2WO_6 with surface oxygen vacancies using an ethylene glycol-assisted solvothermal method and achieved broad-spectrum photocatalytic CO_2 reduction across UV-Vis-NIR for the first time [137]. The introduction of oxygen vacancies creates defect energy levels within the bandgap, extending the photocatalyst's absorption range from ultraviolet to near-infrared (NIR) light, thus covering the entire solar spectrum.

Metal atom vacancies significantly influence light absorption, surface reaction sites, and charge transport. Gao successfully synthesized a gram-level, single-crystal *o*- BiVO_4 layer with vanadium vacancies for the first time by increasing the reaction temperature during the hydrothermal process [138]. Density functional theory (DFT) calculations reveal that vanadium vacancies introduce new defect levels and increase hole concentration near the Fermi level, enhancing both light absorption and electronic conductivity (Figure 6). As a result, the single-crystal *o*- BiVO_4 layer with abundant vanadium vacancies exhibits a high methanol formation rate of $398.3 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ and an apparent quantum efficiency of 5.96% at 350 nm.

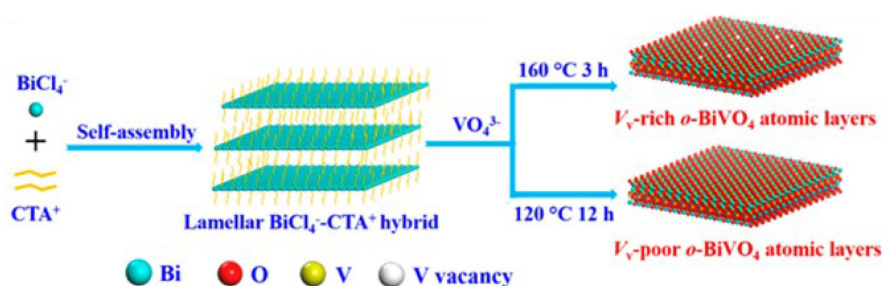


Figure 6. Scheme for the gram-scale synthesis of the V-rich and V-poor *o*- BiVO_4 atomic layers [138]. Reprinted with permission from Ref. [138]. Copyright 2017, American Chemical Society Ltd.

4.2. Microstructure Control

4.2.1. Ultrathin Structures

Atomic-level-thickness oxide-based semiconductors are considered to be an excellent platform for increasing catalytic active sites, increasing CO_2 adsorption and stronger light absorption to promote CO_2 conversion [139].

Taking the orthorhombic Bi_2WO_6 layer as an example, its atomic-scale thickness allows for a high proportion of low-coordinated surface atoms, which serve as catalytic sites for CO_2 reduction reactions. This structure facilitates the easy transfer of photoexcited carriers from the interior to the surface, thereby reducing bulk recombination due to diffusion. When the thickness of the Bi_2WO_6 layer is reduced to a single unit cell, density functional theory (DFT) calculations show an increased density of states (DOS) at the conduction band (CB) edge (Figure 7A,B). Importantly, most of the charge density is concentrated on the surface of the single-unit cell Bi_2WO_6 layer (Figure 7C,D), which means that photoexcited electron–hole pairs reach the surface more quickly than those generated deeper within the material [140].

Liang takes advantage of an intermediate precursor of lamellar Bi-oleate complex successfully synthesized using single-unit-cell Bi_2WO_6 layers [140]. And, through experiments and theoretical calculations, it is proven that the carrier's lifetime is increased and electron–hole separation efficiency is improved. Due to the advantages of ultra-thin structure, these Bi_2WO_6 atomic layers can achieve higher CO_2 adsorption capacity and stronger light absorption, thus exhibiting a methanol generation rate of $75 \mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$ under simulated sunlight, which is more than bulk Bi_2WO_6 (125 times higher). And, the stability is very good; even after 2 days, the catalytic activity will not disappear. Ye

synthesizes ultra-thin nanosheet $\text{Bi}_4\text{O}_5\text{Br}_2$ with a thickness of about 3.7 nm through the glycerol precursor route [141,142], while the thickness of ordinary BiOBr nanosheets is about 65 nm [143]. Due to the ultra-thin and bismuth-rich strategy, $\text{Bi}_4\text{O}_5\text{Br}_2$ photocatalyst under visible light irradiation shows higher CO_2 reduction activity than BiOBr photocatalyst and BiOBr nanosheet photocatalyst [144,145]. Ultra-thin nanosheets increase the generation of CO , and the bismuth-rich strategy enhances the selectivity to CH_4 .

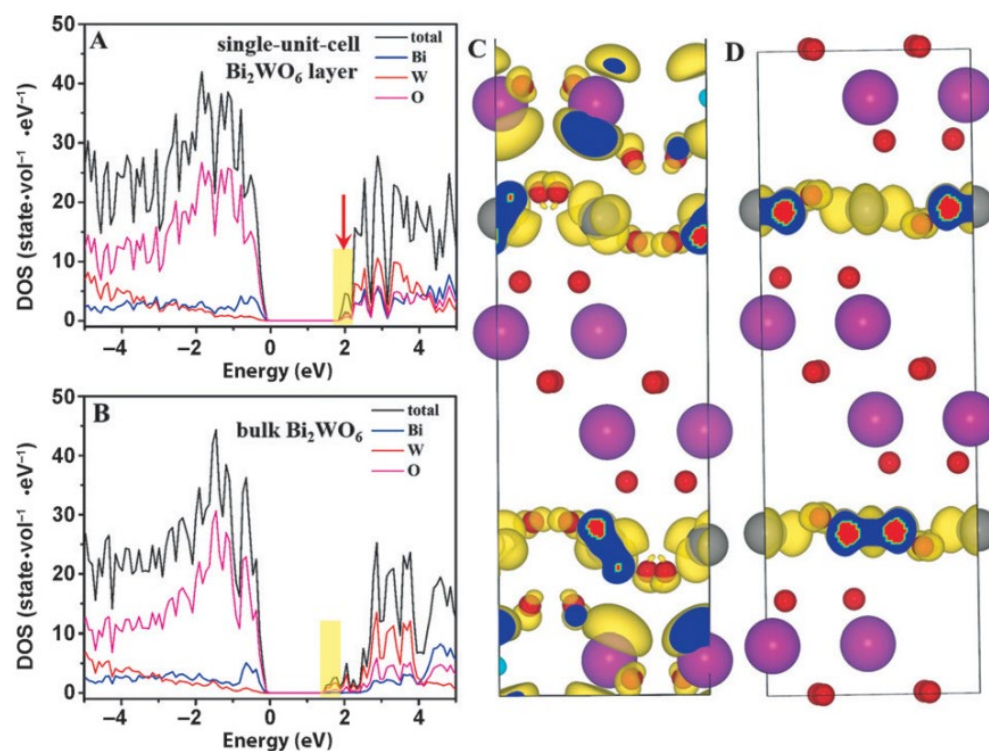


Figure 7. DFT calculations. Calculated density of states of (A) single-unit-cell Bi_2WO_6 layer slab and (B) bulk Bi_2WO_6 slab. Charge density distribution for the conduction band edge of (C) single-unit-cell Bi_2WO_6 layer slab and (D) bulk Bi_2WO_6 slab [140]. Reprinted with permission from Ref. [140]. Copyright 2015, John Wiley and Sons Ltd.

4.2.2. Hollow and Porous Structures

Hollow structure refers to a material with clear boundaries and internal cavities [146]. As a unique series of functional materials, they have low density and high pore volume, as well as shorter mass and charge transfer length. The hollow structure constructed through three-dimensional materials can provide indoor space and utilize the significant reflections of light to help improve photocatalytic performance.

Jin synthesized bismuth-rich hollow $\text{Bi}_4\text{O}_5\text{Br}_2$ graded microspheres using a solvothermal method [147]. The hollow interior increases the specific surface area and generates a strong electric field, which enhances CO_2 adsorption and accelerates the separation of electron–hole pairs (Figure 8). The high bismuth content lowers the conduction band minimum, thereby boosting the reducing power of $\text{Bi}_4\text{O}_5\text{Br}_2$. Together, the hollow structure and bismuth-rich composition give $\text{Bi}_4\text{O}_5\text{Br}_2$ significantly higher photocatalytic CO_2 reduction activity than both BiOBr and solid $\text{Bi}_4\text{O}_5\text{Br}_2$ under solar radiation.

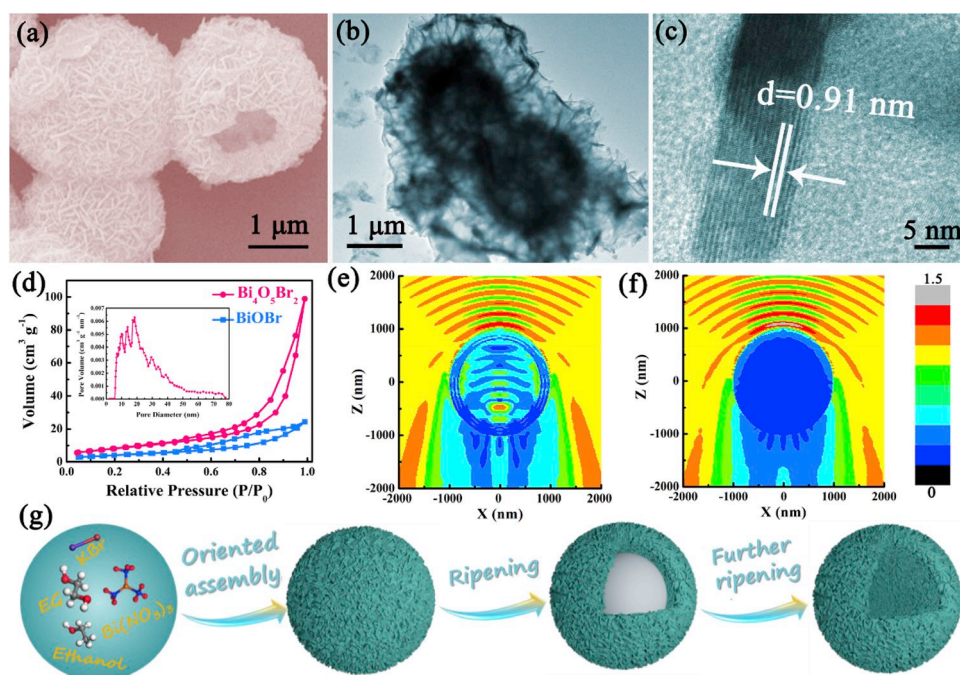


Figure 8. (a,b) SEM and TEM images of hollow $\text{Bi}_4\text{O}_5\text{Br}_2$. (c) HRTEM image of $\text{Bi}_4\text{O}_5\text{Br}_2$ nanosheets from the side view and (d) N_2 adsorption–desorption isotherms. The electric field distribution at the center section (xz plane) of the model of (e) $\text{Bi}_4\text{O}_5\text{Br}_2$ hollow microspheres and (f) BiOBr solid microsphere. (g) Illustration of the formation of $\text{Bi}_4\text{O}_5\text{Br}_2$ hollow spheres [147]. Reprinted with permission from Ref. [147]. Copyright 2015, Elsevier Ltd.

4.3. Crystal Facet Engineering

Crystals grow by reducing their total surface energy. According to the Gibbs–Wulff theorem, facets with higher surface energy grow rapidly but typically occupy a small portion of the surface or disappear. In contrast, facets with lower surface energy grow slowly and remain, ultimately defining the crystal shape. Semiconductor crystals formed under natural or equilibrium conditions often expose less reactive facets, which limits their photocatalytic efficiency [148]. Fortunately, organic or inorganic additives can serve as capping agents, selectively covering high-energy facets and reducing the surface energy of adsorption sites [149]. This allows for the controlled customization and exposure of specific crystal facets, a process known as crystal facet engineering [150].

BiOBr nanosheets dominated by (001) facets are produced through a simple hydrothermal method and different amounts of concentrated nitric acid [151]. The results show that the higher the (001) facets exposure percentage, the better the performance of BiOBr nanosheets in converting CO_2 to CO . This is due to the increase in active sites and more efficient carrier separation and significantly improved reducing power. Ye adjusts the exposed crystal faces of BiOI nanosheets by adjusting the reaction time of the hydrothermal process [152]. It is also proven that the (001) facets of BiOI nanosheets have better photo-generated carrier separation efficiency and a higher CB position.

By controlling the acidity of the reaction solution during the hydrothermal process, Chen produced a series of layered BiOIO_3 single crystals with different ratios of exposed (010) face to (100) face (Figure 9) [153]. Experiments and density functional theory (DFT) confirm that the (010) face on the top surface is enriched by electron-dominated reduction sites and the (100) face on the side surface is concentrated by hole-dominated oxidation sites. And successfully designed the BiOIO_3 crystal with the best thickness and proper ratio of crystal plane, which is about three times that of bulk BiOIO_3 , greatly improving the photocatalytic activity.

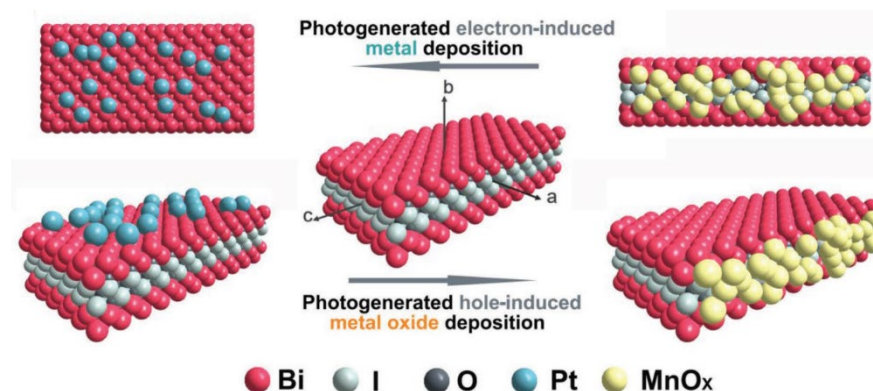


Figure 9. A schematic of the photo deposition of a metal (Pt) or metal oxide (MnOx) on the BiOI₃ nanoplates [153]. Reprinted with permission from Ref. [153]. Copyright 2018, John Wiley and Sons Ltd.

4.4. Bi-Based Composites

In photocatalytic CO₂ reduction, the appropriate loading of cocatalysts serves five key functions: (i) reducing the activation energy or overpotential of the CO₂ reduction reaction on the semiconductor surface; (ii) promoting the separation and migration of photogenerated electron–hole pairs; (iii) improving CO₂ reduction selectivity for specific products; (iv) enhancing photocatalyst stability by consuming photogenerated electrons and holes in a timely manner; and (v) inhibiting side or reverse reactions [9]. However, excessive cocatalyst loading can degrade photocatalytic activity for the following reasons: (i) it may cover the active sites of the photocatalyst, hindering its interaction with CO₂, H₂O, or sacrificial reagents; (ii) it can block incident light, reducing light absorption and thus decreasing the number of photogenerated electron–hole pairs; and (iii) high loading may lead to the formation of larger, unevenly dispersed particles, further decreasing catalytic activity.

4.4.1. Heterojunction Construction

An appropriate heterojunction between two semiconductor photocatalysts is crucial for promoting the separation and transfer of charge carriers. The relative energy levels at the heterojunction interface, in particular, govern the direction and efficiency of electron–hole separation and transfer.

He has formed a series of CdS/BiVO₄ heterogeneous composite materials with different contents of CdS by adjusting the thickness of BiVO₄ [154]. By choosing different scavengers or quenchers and some research to verify that the CdS/BiVO₄ composite adopted a Z-scheme transfer mode under their experiment conditions, the charge transfer mode directly quenches the reductive electrons of BiVO₄ and the oxidative holes of CdS [155–157]. Compared with the original photocatalyst, the CdS/BiVO₄ heterogeneous composite materials increased the activity of reducing CO₂ to CO and CH₄ by 1.5 times and 3 times, respectively, after being irradiated with visible light for 5 h. This increase in photocatalytic activity is attributed to the formation of a Z-scheme heterojunction and the reduction of BiVO₄ thickness. Bai prepared a g-C₃N₄/Bi₄O₅I₂ heterojunction and observed that its CO₂ reduction activity for CO reached 45.6 μmol·g^{−1}·h^{−1}, which is significantly higher than that of either the g-C₃N₄ or Bi₄O₅I₂ photocatalyst alone [158]. Experimental analysis suggests that the I₃[−]/I[−] redox mediator plays a key role in the Indirect Z-scheme of the g-C₃N₄/Bi₄O₅I₂ photocatalytic system. Wang used a simple deposition method to prepare a series of BiOI/g-C₃N₄ photocatalysts [159]. The band edge positions of the g-C₃N₄ and BiOI were determined experimentally, and the results were used to infer the direction of the photogenerated charge transfer across the heterojunction. Liu employed a solvothermal process to prepare an S-type heterojunction composed of DETA-ammoniated α-MnS hollow spheres and Bi₂MoO₆ with a Bi SPR effect [160]. The DETA-organic amine molecule enhances the MnS photocatalyst, facilitating interaction with CO₂

and lowering its activation energy, thereby constructing a highly efficient catalytic system and improving CO₂ reduction efficiency. The Bi/Bi₂MoO₆ S-scheme heterojunction, with an enhanced SPR effect, features a unique electron transport structure that effectively inhibits photocatalyst photo-corrosion and demonstrates high redox capability.

Li employed an in situ deposition method using Au as a bridge to deposit Cd_xZn_{1-x}S@Au on the (010) facet of BiVO₄, thereby constructing a sandwich-structured Cd_xZn_{1-x}S@Au/BiVO₄ Z-scheme photocatalyst [161]. In this system, photogenerated electrons in the BiVO₄ migrate unidirectionally to the Au nanoparticles via the Schottky junction, effectively preventing reverse electron flow. These electrons are then captured by the excited holes in the Cd_xZn_{1-x}S photocatalyst. Additionally, Zn doping enhances the redox capability and improves charge carrier separation. Compared to CdS and CdS@Au/BiVO₄, Cd_xZn_{1-x}S@Au/BiVO₄ demonstrates superior photocatalytic activity for CO₂ reduction under visible light irradiation.

Yuan employed an electrostatic self-assembly method to prepare Bi₂WO₆/TiO₂ heterogeneous composite materials (Figure 10) [162]. Experimental results show that this photocatalyst follows the Z-scheme charge transfer mechanism (Figure 10). The combination of electrons from the Bi₂WO₆ conduction band (CB) and holes from the TiO₂ valence band (VB) enhances hole availability on the VB of Bi₂WO₆ for the oxidation of H₂O, which produces more protons (H⁺) for CH₄ formation. Additionally, the selectivity and yield of CO₂ reduction to CH₄ are improved. What is interesting is that Yuan's comprehensive study of Bi₂WO₆/TiO₂ photocatalyst under N₂ and CO₂ atmospheres found that when there is a large amount of carbonaceous residue on the photocatalyst, the decomposition of carbonaceous residue will be greatly inhibited. In addition, the presence of carbon residues on the sample will interfere with the measurement of CO₂ photocatalytic reduction activity. In the end, the yield of CO₂ reduction and precipitation CO is as high as 61.11 µmol·g⁻¹·h⁻¹.

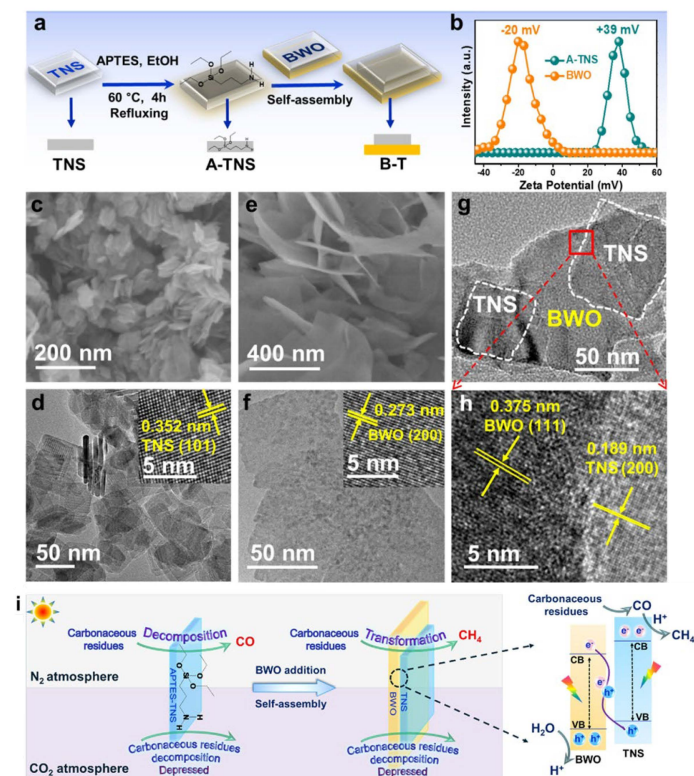


Figure 10. (a) Flowchart for the fabrication of A-TNS and B-T. (b) Zeta potentials for Bi₂WO₆ and TiO₂. (c–f) SEM and TEM images for TiO₂ and Bi₂WO₆, respectively. (g,h) Insets of TEM and HRTEM images for Bi₂WO₆/TiO₂ photocatalyst. (i) Schematic diagram of the reaction process [162]. Reprinted with permission from Ref. [162]. Copyright 2018, Elsevier Ltd.

4.4.2. Electron Transporting Material Loading Ions Grafting

Unlike surface lattice doping or single-atom doping, ion grafting involves attaching external anions or cations to the surface atoms of the photocatalyst, creating a localized polarization field and altering its surface chemical state. However, due to the selective transfer of surface electrons and holes between the exposed surface atoms and the grafted ions, excessive ion encapsulation can hinder the exposure of the photocatalyst's surface atoms. Therefore, in order to better carry out CO₂ photoreduction, an appropriate graft ion concentration should be considered. In addition, the type of ion has a relatively large impact on the photocatalyst. For example, halogens have relatively large electronegativity, when they form bonds with surface metal cations, tending to cause asymmetric distribution of charges or co-catalysts exhibiting a CO yield 73 times higher than that of the unmodified photocatalyst [163].

Hao prepared a layered photocatalyst Bi₂O₂(OH)(NO₃) (BON) by substituting surface halogen ions for surface hydroxyl groups and then fixing them on Bi atoms, as shown in Figure 11a–d [164]. This action promotes local charge separation, activates hydroxyl groups, greatly promotes the adsorption of CO₂ molecules and protons, and further promotes CO₂ conversion. Among the three series of BON-X (X = Cl, Br, and I) catalysts, BON-Br has no sacrificial agent.

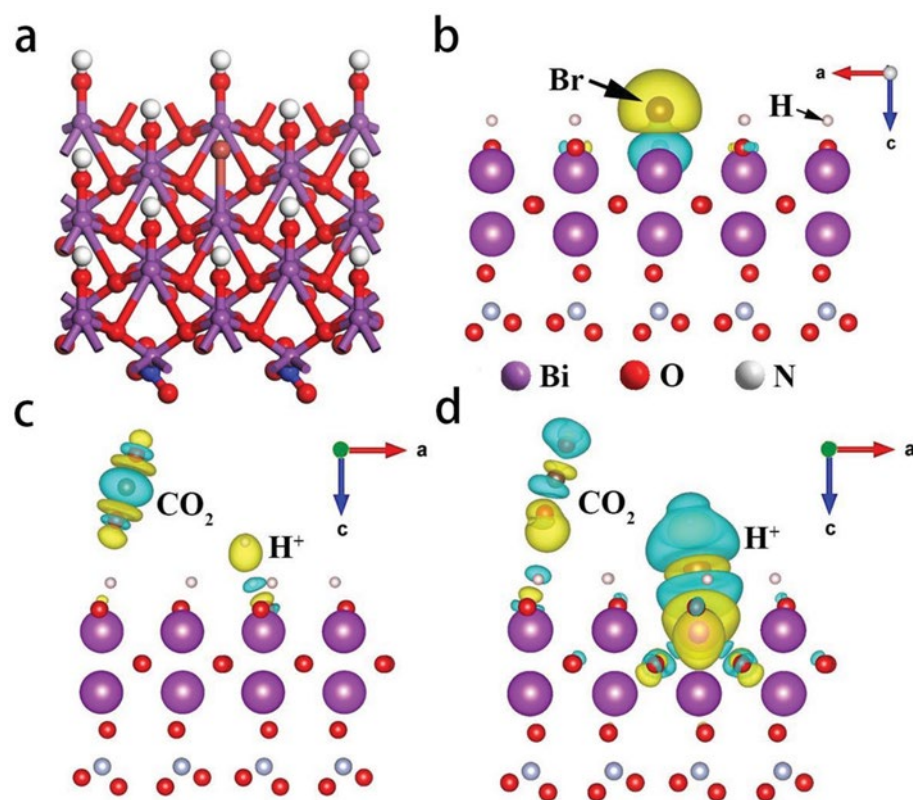


Figure 11. (a) Schematic crystal structure of BON-Br. (b–d) Charge difference of BON-Br [164]. Reprinted with permission from Ref. [164]. Copyright 2019, John Wiley and Sons Ltd.

Loading Metal

Inorganic precious metals have a higher work function, which means that inorganic precious metals generally have lower Fermi levels (E_F) and strong electron extraction capabilities. Taking Pt as an example, Pt has the highest work function (5.65 eV). Loading Pt on the surface of photocatalysts can greatly improve electron–hole separation and migration, thereby enhancing their photocatalytic performance. However, Pt is easy to

capture and induce electrons to generate H_2 , and the generation of H_2 is a competitive reaction with the reduction of CO_2 . In addition, CO will be firmly bound to the Pt metal, resulting in photocatalyst poisoning, and it is not easy to generate CO. It is very important to choose the right metal.

Raja deposited nano-sized Pd particles on the surface of $Bi_2Ti_3O_9$ photocatalyst through an ultrasonic-assisted incipient wetness technique [165], reducing CO_2 to $HCOOH$, which is twice as active as unloaded Pd. Bai innovatively supported reduction and oxidation co-catalysts on the surface of the photocatalyst, which not only provides active sites for the reduction and oxidation of the reaction but also extracts photo-generated electrons and holes to the surface [166]. Bai co-loaded Au and MnOx on BiOI, and its activity reached $42.9 \mu mol \cdot g^{-1} \cdot h^{-1}$, which was seven times that of the original photocatalyst. Experiments show that the photon absorption efficiency of Au/MnOx/BiOI photocatalyst and BiOI photocatalyst are at the same level, and the improvement of photocatalytic activity comes from the improvement of the efficiency of photo-induced carrier and hole separation. The catalytic activity of the Au/BiOI photocatalyst is 2.1 times that of the MnOx/BiOI photocatalyst, which proves that the electron-withdrawing Au plays a more important role in the improvement of the photocatalytic activity than the hole-absorbing MnOx promoter.

Yang was the first to use metallic bismuth, rather than precious metals, as a promoter of photocatalytic CO_2 reduction, as shown in Figure 12 [167]. Compared to the original photocatalyst, CO yield was significantly improved, increasing by about 4.8 times. While precious metals are difficult to deposit through in situ light, metallic Bi can be deposited as quantum dots under in situ light conditions, with an average size of approximately 5 nm. On one hand, Bi at the quantum dot level is unstable in air and challenging to store. On the other hand, unstable Bi can be stabilized in the form of Bi/ Bi_2O_3 quantum dots. During photocatalytic CO_2 reduction, white Bi/ Bi_2O_3 (primarily Bi_2O_3) can easily convert into gray Bi/ Bi_2O_3 composites (primarily Bi), improving the photocatalytic CO_2 reduction rate.

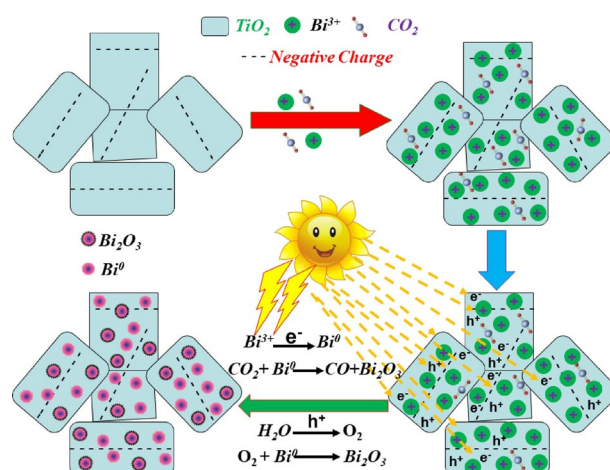


Figure 12. Schematic representation of the photo deposition process of Bi/ Bi_2O_3 quantum dots on the surface of TiO_2 nanosheets [167]. Reprinted with permission from Ref. [167]. Copyright 2018, Elsevier Ltd.

4.5. Co-Strategies

A single strategy cannot address both the thermodynamic and kinetic challenges of CO_2 photoreduction, as well as the inherent defects of photocatalysts. Therefore, combining multiple strategies is essential to enhance photocatalytic performance.

Chen achieved highly efficient CO_2 photoreduction by synthesizing $BiOI/O_3$ single-crystal nanobelts with macroscopic spontaneous polarization and surface oxygen vacancies [168]. By controlling the directional growth of $BiOI/O_3$ nanoribbons along the (001)

direction, a large number of well-aligned IO_3 polar units are formed, enhancing the macroscopic polarized electric field and promoting the rapid separation and migration of charges from the bulk to the surface (Figure 13). Additionally, the surface oxygen vacancies create a local electric field, inhibiting the recombination of holes and photogenerated electrons and enhancing CO_2 adsorption on the photocatalyst surface. The BiOIO_3 nanobelt reduces CO_2 to CO at a rate of $17.33 \mu\text{mol} \cdot \text{g}^{-1} \cdot \text{h}^{-1}$ without any sacrificial agent or promoter, making it one of the most efficient photocatalysts for CO_2 reduction.

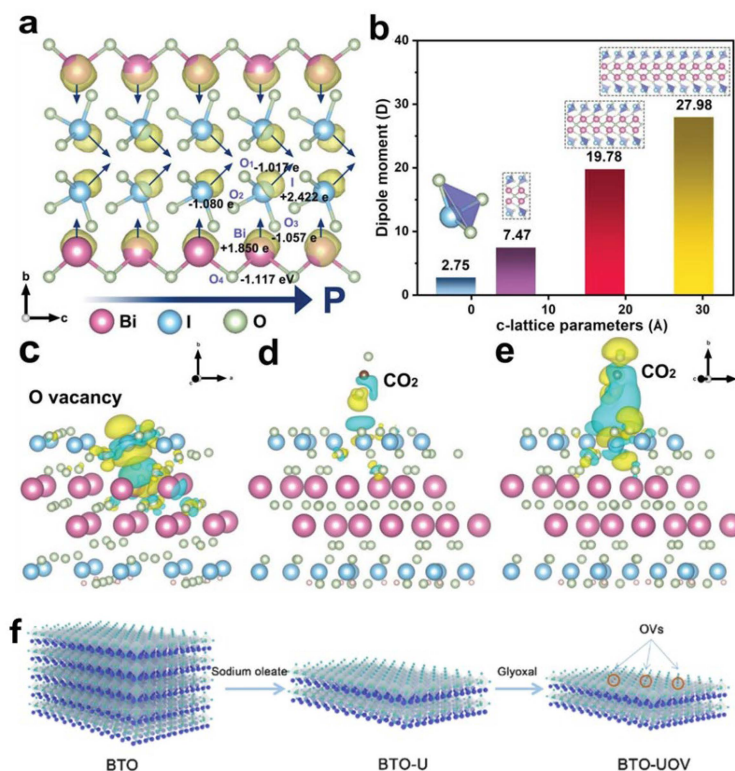


Figure 13. (a) The electron localization function of BiOIO_3 . (b) The dipole moment (Z-axis) of IO_3 and the BiOIO_3 unit cells with different c-lattice lengths. (c) Charge difference of BiOIO_3 with OVs. (d) Charge difference of CO_2 adsorbed on BiOIO_3 and (e) BiOIO_3 with OVs (charge accumulation is in yellow and depletion is in blue) [168]. (f) Schematic illustration of the formation of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ [169]. Reprinted with permission from Refs. [168,169]; Copyright 2020, John Wiley and Sons Ltd. and Elsevier Ltd.

Liu, from the same group, solved the problems of insufficient carrier separation and weak CO_2 adsorption by preparing two-dimensional $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ ultra-thin nanosheets rich in oxygen vacancies [169]. The selective photo deposition experiment of Pt on $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ showed that the ultra-thin structure can shorten the migration distance of photogenerated electrons from the bulk to the surface, which is beneficial for quickly participating in the CO_2 reduction reaction. Oxygen vacancies lead to a huge improvement in the surface state and the electronic structure, as well as improving the efficiency of CO_2 adsorption, light absorption, and charge separation (Figure 13f). Therefore, in terms of the CO precipitation rate, the best activity of $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheets is 3.2 times that of the original photocatalyst.

The combination of atomic layer photocatalysts and oxygen vacancies significantly improves the limitations of poor light absorption, slow electron–hole separation, and high CO_2 activation barriers. Bi synthesized a Bi_2MoO_6 photocatalyst with an ultra-thin two-dimensional structure and surface defects using a template-oriented strategy (Figure 14a–f) [170]. The engineered “Bi–O” vacancy pairs modify the local atomic and electronic structure of the photocatalyst, serving as charge separation centers to promote electron–hole separation. The defective ultra-thin structure enhances CO_2 adsorption and activation and CO desorption. Un-

der light irradiation, the photocatalytic activity of the defective ultra-thin Bi_2MoO_6 nanosheets was 2.55 times higher than that of the original photocatalyst. Wu fabricated BiOBr atomic layers with abundant surface oxygen vacancies (Figure 14g) [171]. Both experimental and theoretical studies confirmed that the new defect levels introduced by oxygen vacancies extend light absorption into the visible light region, while charge delocalization around the vacancies aids in CO_2 activation to form COOH^* intermediates. The atomic layer structure also enhances charge separation and increases the number of surface catalytic sites [172]. Finally, the oxygen vacancies and the atomic layer together enhance the CO_2 photoreduction performance of BiOBr, which is 20 times and 24 times that of the BiOBr atomic layer and bulk BiOBr, respectively. Bi prepared atomically layered $\text{Bi}_3\text{O}_4\text{Br}$ photocatalysts decorated with isolated single atom Co [173]. The atomically layered structure reduces the possibility of carrier recombination while providing more active sites to promote the reaction. Isolated single atom Co in $\text{Bi}_3\text{O}_4\text{Br}$ is beneficial for carrier and hole separation and CO_2 adsorption and activation. Its CO_2 photoreduction performance is 4 times and 32 times higher than that of atomically layered $\text{Bi}_3\text{O}_4\text{Br}$ and bulk $\text{Bi}_3\text{O}_4\text{Br}$.

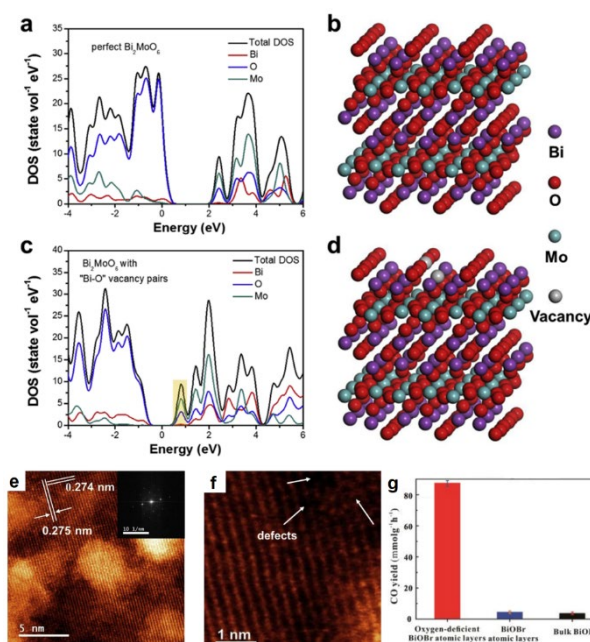


Figure 14. Calculated density of states of (a) perfect Bi_2MoO_6 and (c) Bi_2MoO_6 with “Bi-O” vacancy pairs. Structure model of (b) perfect Bi_2MoO_6 and (d) Bi_2MoO_6 with “Bi-O” vacancy pairs. (e) Atomic-resolution STEM-ADF image showing the lattice parameters of Bi_2MoO_6 and (f) the enlarged image confirm the presence of abundant atomic defects [170]. (g) CO yield under a 300 W Xe lamp with a 400 nm cut filter to filter UV radiation for oxygen-deficient BiOBr atomic layers, BiOBr atomic layers, and bulk BiOBr [171].

Building on the preceding discussion of the structural characteristics of Bi-based semiconductors and the associated strategies for performance enhancement, such as defect engineering, microstructure regulation, crystal facet engineering, and heterojunction construction, Table 1 summarizes representative studies reported in recent years. This table compares the photocatalytic CO_2 reduction performance of various Bi-based photocatalysts under different reaction conditions, including reactor configuration, light source, reaction parameters, product distribution, and production rates. When examined in conjunction with the preceding analysis, Table 1 enables a more intuitive assessment of how different structural design and modulation strategies affect photocatalytic activity and product selectivity, thereby providing useful guidance for the rational design of efficient Bi-based photocatalysts.

Table 1. Summary of recent studies on the photocatalytic performance of Bi-based photocatalysts.

Photocatalyst	Strategy	Reactor Type	Catalyst Mass	Illumination	Temperature	CO ₂ Partial Pressure/Flow	Run Time	Products and Production Rate ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Reference Photocatalyst (Production Rate, $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Refs.
BiOBr	Crystal facet engineering	500 mL closed batch system	50 mg	300 W xenon lamp	20 °C	1 atm	Not reported	CO (gas): 4.5	CO (gas): 1.6	[103]
BiOBr	Co-strategies	Not reported	50 mg	300 W xenon lamp ($\lambda > 400$ nm)	Not reported	50 m/min	5 h	CO (gas): 87.4	CO (gas): 4.7 CO (bulk): 3.6	[122]
BiOBr	Microstructure control	Not reported	150 mg	300 W xenon lamp ($\lambda > 400$ nm)	15–45 °C	Not reported	Not reported	CO (gas): 2.67 CH ₄ (gas): 0.16	CO (gas): 1.68 CH ₄ (gas): 0.16	[98]
BiOI ₃	Crystal facet engineering	500 mL closed batch system	50 mg	300 W xenon lamp	20 °C	1 atm	Not reported	CO (gas): 5.42	CO (gas): 1.77	[105]
BiOI ₃	Co-strategies	Not reported	30 mg	300 W xenon lamp	Not reported	Not reported	1 h	CO (gas): 17.33	CO (gas): 1.68	[119]
BiVO ₄	Doping	Not reported	150 mg	A 25 W ultraviolet lamp with specific wavelength of 254 nm	Ambient temperature	Not reported	1 h	CH ₄ (gas): 23.8	CH ₄ (gas): 8.3	[124]
BiVO ₄	Vanadium vacancy	Not reported	70 mg	300 W xenon lamp	0 °C	Not reported	10 h	CH ₃ OH (liquid): 398.3	CH ₃ OH (liquid): 284.5	[95]
BiVO ₄	Heterojunction construction	Not reported	20 mg	300 W xenon lamp	Not reported	Not reported	1 h	CO (gas): 0.39 CH ₄ (gas): 1.75	CO (gas): 0.26 CH ₄ (gas): 0.59	[106]
BiVO ₄	Different crystal phases	Not reported	Not reported	A fluorescent lamp (36 W)	30 °C	1 atm	Not reported	CH ₃ OH (gas): 1.35 C ₂ H ₅ OH (liquid): 1.73	CH ₃ OH (gas): 0.45 C ₂ H ₅ OH (liquid): 0.45	[125]
BiVO ₄	Heterojunction construction	Not reported	50 mg	300 W xenon lamp ($\lambda > 400$ nm)	Not reported	Not reported	Not reported	CO (gas): 2.2	CO (gas): 0.7	[113]
Bi ₂ WO ₆	Oxygen vacancy	Continuous gas flow reactor	120 mg	A Xe lamp (500W) including UV ($\lambda < 400$ nm), Vis ($\lambda > 400$ nm), NIR ($\lambda > 700$ nm), and simulated solar light	Not reported	1 atm	8 h	CH ₄ (gas): 13.9	CH ₄ (gas): 4.9	[94]
Bi ₂ WO ₆	Microstructure control	Not reported	120 mg	300 W xenon lamp	20 °C	Not reported	1 h	CH ₃ OH (liquid): 75.0	CH ₃ OH (liquid): 0.6	[97]
Bi ₂ WO ₆	Heterojunction construction	Not reported	20 mg	300 W xenon lamp (780 nm $> \lambda > 320$ nm)	25 °C	Not reported	1 h	CO (gas): 25.8 CH ₄ (gas): 10.8	CO (gas): 2.6 CH ₄ (gas): 0.7	[103]
Bi ₂ O ₂ (OH)(NO ₃)	Ion grafting	Not reported	200 mg	300 W xenon lamp	Ambient temperature	Not reported	Not reported	CO (gas): 8.1	CO (gas): 0.1	[115]
BiOI	Loading metal	350 mL closed batch system	20 mg	300 W high-pressure xenon lamp	20 °C	1 atm	Not reported	CO (gas): 42.9	CO (gas): 6.13	[117]
BiOI	Crystal facet engineering	500 mL closed batch system	150 mg	300 W high-pressure xenon lamp	20 °C	1 atm	Not reported	CO (gas): 5.18 CH ₄ (gas): 1.78	CO (gas): 1.52 CH ₄ (gas): 1.50	[104]
BiOI	Oxygen vacancy	Not reported	150 mg	300 W high-pressure xenon lamp	20 °C	1 atm	1 h	CO (gas): 4.10 CH ₄ (gas): 0.42	CO (gas): 0.51 CH ₄ (gas): 0.19	[126]

Table 1. Cont.

Photocatalyst	Strategy	Reactor Type	Catalyst Mass	Illumination	Temperature	CO ₂ Partial Pressure/Flow	Run Time	Products and Production Rate ($\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Reference Photocatalyst (Production Rate, $\mu\text{mol}\cdot\text{g}^{-1}\cdot\text{h}^{-1}$)	Refs.
BiOI	Heterojunction construction	Not reported	50 mg	300 W xenon lamp ($\lambda > 400$ nm)	Ambient temperature	1 atm	9 h	CO (gas): 4.86 CH ₄ (gas): 0.18	CO (gas): 0 CH ₄ (gas): 0	[111]
Bi ₄ O ₅ I ₂	Heterojunction construction	Not reported	100 mg	300 W xenon lamp ($\lambda > 400$ nm)	45	Not reported	2 h	CO (gas): 45.6	CO (gas): 19.8	[110]
Bi ₄ O ₅ I ₂	Bismuth-rich strategy	350 mL closed batch system	100 mg	300 W high-pressure xenon lamp with 400 nm cut-off filters	20 °C	1 atm	1 h	CO (gas): 19.82 CH ₄ (gas): 0.22	CO (gas): 0.70 CH ₄ 0.27	[127]
Bi ₄ Ti ₃ O ₁₂	Co-strategies	Not reported	20 mg	300 W xenon lamp	20–35 °C	Not reported	12 h	CO (gas): 11.7	CO (gas): 3.6	[120]
Bi ₂ Ti ₃ O ₉	Loading metal	500 mL photocatalytic reactor with quartz window (liquid-phase)	20 mg	300 W solar simulator with AM 1.5 filter	20–40 °C	CO ₂ -saturated 0.1 M H ₂ SO ₄ ; CO ₂ bubbling 150 mL·min ^{−1}	8 h (rate reported for first 8 h)	HCOOH (liquid): 110 (first 8 h)	HCOOH (liquid): 23 (first 8 h)	[116]
Bi ₂ MoO ₆	Co-strategies	Not reported	70 mg	300 W xenon lamp	Ambient temperature	1 atm	1 h	CO (gas): 3.6	CO (gas): 1.4	[121]
Bi ₂ MoO ₆	Heterojunction construction	Not reported	50 mg	300 W xenon lamp	20 °C	Not reported	3 h	CO (gas): 61.1	CO (gas): 12.2	[112]
BiOCl	Oxygen vacancy	Not reported	70 mg	500 W xenon lamp	Not reported	Not reported	Not reported	CO (gas): 8.1 CH ₄ (gas): 1.2	CO (gas): 0 CH ₄ (gas): 0	[90]
Bi ₄ O ₅ Br ₂	Microstructure control	350 mL closed batch system	50 mg	300 W high-pressure xenon lamp	20 °C	2 atm	12 h	CO (gas): 3.2 CH ₄ (gas): 0.5	CO (gas): 0 CH ₄ (gas): 0	[100]
Bi ₄ O ₅ Br ₂	Bismuth-rich strategy	Not reported	80 mg	300 W xenon lamp ($\lambda > 400$ nm)	15–45 °C	Not reported	Not reported	CO (gas): 2.73 CH ₄ (gas): 2.04	CO (gas): 1.68 CH ₄ (gas): 0.16	[98]
Bi ₃ O ₄ Br	Co-strategies	500 mL closed batch system	30 mg	300 W xenon lamp	5 °C	Not reported	Not reported	CO (gas): 107.1	CO (gas): 3.3	[123]
PbBiO ₂ Br	Oxygen vacancy	Not reported	20 mg	300 W Xe lamp with a 400 nm cut-off filter used as the light source to trigger the photocatalyst	10 °C	CO ₂ in the system was adjusted to 80 kPa	Not reported	CO (gas): 4.58	CO (gas): 0.42	[92]
Bi ₂ S ₃	Heterojunction construction	Not reported	200 mg	500 W xenon lamp (700 nm $> \lambda > 200$ nm)	Not reported	Not reported	Not reported	CH ₃ OH (liquid): 122.6	CH ₃ OH (liquid): 61.3	[67]
Bi ₂ O ₃	Loading metal	Not reported	120 mg	A Xe lamp (300 W)	60 °C	Not reported	6 h	CO (gas): 4.8	CO (gas): 0	[118]
Bi ₅ O ₇ I	Bismuth-rich strategy	350 mL closed batch system	100 mg	300 W high-pressure xenon lamp with 400 nm cut-off filters	35 °C	1 atm	1 h	CO (gas): 1.73 CH ₄ (gas): 0.18	CO (gas): 0.70 CH ₄ 0.27	[127]
Bi ₂ Sn ₂ O ₇	Oxygen vacancy	Not reported	20 mg	300 W xenon lamp	5 °C	Not reported	Not reported	CO (gas): 14.88	CO (gas): 1.84	[93]
Bi ₁₂ O ₁₇ C ₁₂	Oxygen vacancy	Not reported	Not reported	A Xe lamp (300 W)	Not reported	Not reported	Not reported	CO (gas): 48.6	CO (gas): 2.9	[91]

5. Outlook

This review summarizes the main performance of bismuth-based semiconductors in photocatalytic CO₂ reduction and the adaptation strategies of bismuth-based catalysts to improve the yield of valuable energy. In addition, the fundamentals and challenges of CO₂ photoreduction and common bismuth-based semiconductors are also introduced. Although many achievements have been made in designing CO₂ reduction photocatalysts with high activity and product selectivity, many explorations and approaches are still in their infancy. Many challenges remain for the further development of this field.

The stability of bismuth-based semiconductors in catalytic reactions is as important as high activity. However, the reasons for deactivation are diverse, including the accumulation of reaction intermediates on the photocatalyst surface, the dissociation of intermediates as by-products, the self-oxidation of bismuth groups, the loss of active oxidation states, and many other reasons. Attempts to make improvements in catalyst stability have been made through a variety of approaches, such as the use of hole scavengers, the construction of heterostructures to retain the desired oxidation state, and the removal of intermediates through heat treatment and other methods. However, there is still a great deal of work to be done to ensure long-term stability and prevent catalyst degradation.

Most of the photocatalysts reported in the literature produce C1 products, such as CO and CH₄, with limited studies focused on enhancing C₂+selectivity. Given the higher value of C₂+products, it is more desirable to pursue the formation of C₂+ compounds, such as ethylene, ethanol, and higher alcohols, instead of CO, CH₄, and formates. To achieve C-C coupling and form C₂+ products, several concrete routes need to be considered. One promising approach is tuning surface CO coverage. By controlling the coverage of *CO on the catalyst surface, it is possible to regulate the reaction pathways and shift the selectivity toward C₂+ products. This can be achieved by adjusting the adsorption strength of *CO on the photocatalyst, where an optimal binding strength will facilitate the coupling of *CO intermediates into larger carbon chains while avoiding excessive desorption or further hydrogenation of C1 products.

Another effective strategy to enhance C-C coupling is the use of dual-site catalysts. These catalysts can be designed with two distinct active sites: one for CO₂ adsorption and the other for facilitating C-C bond formation. This spatial separation of reactions allows for more efficient product formation, especially for C₂+ compounds. Additionally, tandem junctions involving two semiconductors with complementary properties can also promote C-C coupling. By combining a material that efficiently reduces CO₂ to *CO with another that promotes C-C coupling, these junctions provide a favorable environment for efficient charge separation and enhanced product selectivity.

In terms of in situ and operando tools, several techniques are crucial for understanding the reaction mechanisms and the role of intermediates in CO₂ reduction. DRIFTS (Diffuse Reflectance Infrared Fourier Transform Spectroscopy) is particularly valuable for tracking surface-bound intermediates, such as *COOH, *CO, *CHO, and *HCO, during the photocatalytic process. This technique helps identify how intermediates evolve and whether they are stabilized on the catalyst surface. EPR (Electron Paramagnetic Resonance) is effective in identifying reactive species, such as radicals and unpaired electrons, which play a crucial role in electron transfer and charge separation processes. Raman spectroscopy provides insight into the vibrational modes of surface intermediates and allows for the detection of changes in bonding as the reaction progresses. Finally, AP-XPS (Ambient Pressure X-ray Photoelectron Spectroscopy) is essential for studying the catalyst's surface chemistry under reaction conditions. This technique can reveal the oxidation states of the catalyst, providing direct information about the electronic structure and the formation of key intermediates during CO₂ reduction.

A comprehensive, reliable, and stable product testing system is also required to accurately detect and quantify all possible products in CO₂ photoreduction. While CO, CH₄, H₂, and O₂ are the most commonly studied products, other potential products, such as HCOOH, CH₃OH, and C₂+ compounds, are often overlooked. The development of advanced product detection systems capable of accurately measuring these products at ultra-low concentrations is crucial for advancing the study of reaction mechanisms and improving product selectivity.

Author Contributions: Conceptualization, Y.L. and J.Y.; methodology, J.Y.; software, W.H. (Wei He); validation, W.H. (Wei He), W.H. (Wenxin Hu), and F.L.; formal analysis, H.G.; investigation, Z.Y.; resources, Z.Y.; data curation, Y.L.; writing—original draft preparation, J.Y.; writing—review and editing, Y.L.; visualization, Y.L.; supervision, Y.L.; project administration, Y.L.; funding acquisition, J.Y. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by the 2025 Natural Science Foundation of Inner Mongolia Autonomous Region [2025QN05125]. The authors gratefully acknowledge this financial support.

Data Availability Statement: The data presented in this study are available upon request from the corresponding author.

Conflicts of Interest: The authors declare no conflicts of interest. The funders had no role in the design of the study; in the collection, analyses, or interpretation of data; in the writing of the manuscript; or in the decision to publish the results.

References

1. Chae, S.Y.; Lee, S.Y.; Han, S.G.; Kim, H.; Ko, J.; Park, S.; Joo, O.-S.; Kim, D.; Kang, Y.; Lee, U.; et al. A perspective on practical solar to carbon monoxide production devices with economic evaluation. *Sustain. Energy Fuels* **2020**, *4*, 199–212. [\[CrossRef\]](#)
2. Guo, K.; Hussain, I.; Jie, G.; Fu, Y.; Zhang, F.; Zhu, W. Strategies for improving the photocatalytic performance of metal-organic frameworks for CO₂ reduction: A review. *J. Environ. Sci.* **2023**, *125*, 290–308. [\[CrossRef\]](#)
3. Modak, A.; Bhanja, P.; Dutta, S.; Chowdhury, B.; Bhaumik, A. Catalytic reduction of CO₂ into fuels and fine chemicals. *Green Chem.* **2020**, *22*, 4002–4033. [\[CrossRef\]](#)
4. Ray, B.; Churipard, S.R.; Peter, S.C. An overview of the materials and methodologies for CO₂ capture under humid conditions. *J. Mater. Chem. A* **2021**, *9*, 26498–26527. [\[CrossRef\]](#)
5. Kim, D.; Sakimoto, K.K.; Hong, D.; Yang, P. Artificial photosynthesis for sustainable fuel and chemical production. *Angew. Chem. Int. Ed.* **2015**, *54*, 3259–3266. [\[CrossRef\]](#)
6. Lewis, N.S.; Nocera, D.G. Powering the planet: Chemical challenges in solar energy utilization. *Proc. Natl. Acad. Sci. USA* **2006**, *103*, 15729–15735. [\[CrossRef\]](#)
7. Li, K.; Peng, B.; Peng, T. Recent Advances in Heterogeneous Photocatalytic CO₂ Conversion to Solar Fuels. *ACS Catal.* **2016**, *6*, 7485–7527. [\[CrossRef\]](#)
8. Singhal, N.; Kumar, U. Noble metal modified TiO₂: Selective photoreduction of CO₂ to hydrocarbons. *Mol. Catal.* **2017**, *439*, 91–99. [\[CrossRef\]](#)
9. Ran, J.; Jaroniec, M.; Qiao, S.Z. Cocatalysts in Semiconductor-based Photocatalytic CO₂ Reduction: Achievements, Challenges, and Opportunities. *Adv. Mater.* **2018**, *30*, 1704649. [\[CrossRef\]](#)
10. Fu, J.; Jiang, K.; Qiu, X.; Yu, J.; Liu, M. Product selectivity of photocatalytic CO₂ reduction reactions. *Mater. Today* **2020**, *32*, 222–243. [\[CrossRef\]](#)
11. Marszewski, M.; Cao, S.; Yu, J.; Jaroniec, M. Semiconductor-based photocatalytic CO₂ conversion. *Mater. Horiz.* **2015**, *2*, 261–278. [\[CrossRef\]](#)
12. Olah, G.A.; Prakash, G.K.; Goepfert, A. Anthropogenic chemical carbon cycle for a sustainable future. *J. Am. Chem. Soc.* **2011**, *133*, 12881–12898. [\[CrossRef\]](#) [\[PubMed\]](#)
13. Fujishima, A.; Honda, K. Electrochemical photolysis of water at a semiconductor electrode. *Nature* **1972**, *238*, 37. [\[CrossRef\]](#) [\[PubMed\]](#)
14. Halmann, M. Photoelectrochemical reduction of aqueous carbon dioxide on p-type gallium phosphide in liquid junction solar cells. *Nature* **1978**, *275*, 115–116. [\[CrossRef\]](#)

15. Zhang, Z.; Wang, B.; Zhao, H.-B.; Liao, J.-F.; Zhou, Z.-C.; Liu, T.; He, B.; Wei, Q.; Chen, S.; Chen, H.-Y.; et al. Self-assembled lead-free double perovskite-MXene heterostructure with efficient charge separation for photocatalytic CO₂ reduction. *Appl. Catal. B Environ.* **2022**, *312*, 121358. [CrossRef]
16. Qian, X.; Yue, D.; Tian, Z.; Reng, M.; Zhu, Y.; Kan, M.; Zhang, T.; Zhao, Y. Carbon quantum dots decorated Bi₂WO₆ nanocomposite with enhanced photocatalytic oxidation activity for VOCs. *Appl. Catal. B Environ.* **2016**, *193*, 16–21. [CrossRef]
17. Ni, B.; Jiang, H.; Guo, W.; Xu, Q.; Min, Y. Tailoring the oxidation state of metallic TiO through Ti₃₊/Ti₂₊ regulation for photocatalytic conversion of CO₂ to C₂H₆. *Appl. Catal. B Environ.* **2022**, *307*, 121141. [CrossRef]
18. Yang, H.; Zhou, J.; Duan, Z.; Liu, X.; Deng, B.; Fang, J.; Xu, W. Amorphous TiO₂ beats P₂₅ in visible light photo-catalytic performance due to both total-internal-reflection boosted solar photothermal conversion and negative temperature coefficient of the forbidden bandwidth. *Appl. Catal. B Environ.* **2022**, *310*, 121299. [CrossRef]
19. Zhang, H.; Yang, X.; Gao, G.; Yan, J.; Zhao, M.; Su, H. An efficient catalyst of CuPt/TiO₂ for photocatalytic direct dehydrogenation of methanol to methyl formate at ambient temperature†. *Catal. Sci. Technol.* **2022**, *12*, 773–785. [CrossRef]
20. Duan, M.; Hu, C.; Duan, D.; Chen, R.; Wang, C.; Wu, D.; Xia, T.; Liu, H.; Dai, Y.; Long, R.; et al. Ppm-level Cu dopant on ultrathin Pd nanosheets/TiO₂ for highly enhanced photocatalytic alcoholysis of epoxides. *Appl. Catal. B Environ.* **2022**, *307*, 121211. [CrossRef]
21. Anandkumar, M.; Sudarsan, S.; Naganaboina, V.R.; Bandari, N.K.; Litvinyuk, K.S.; Singh, S.G.; Trofimov, E.A. High-Entropy (Ce_{0.2}Pr_{0.2}Zn_{0.2}Nd_{0.2}Tb_{0.2})₂Zr₂O₇ Zirconate Pyrochlore: A Promising Photocatalyst for Diverse Environmental Applications. *Nanomaterials* **2025**, *15*, 1668. [CrossRef]
22. Huo, Y.; Zhang, P.; Chi, J.; Fang, F.; Song, Y.; Sun, D. Surface Functionalization and Defect Construction of SnO₂ with Amine Group for Enhanced Visible-Light-Driven Photocatalytic CO₂ Reduction. *Adv. Energy Mater.* **2024**, *14*, 2304282. [CrossRef]
23. Huang, K.; Liang, G.; Sun, S.; Hu, H.; Peng, X.; Shen, R.; Li, X. Interface-induced charge transfer pathway switching of a Cu₂O-TiO₂ photocatalyst from p-n to S-scheme heterojunction for effective photocatalytic H₂ evolution. *J. Mater. Sci. Technol.* **2024**, *193*, 98–106. [CrossRef]
24. Wang, R.; Zhang, M.; Liu, J.; Wu, X.; Zhang, S.; Zhong, Q.; Yao, J. Defect-phase engineered NiTi-TiO₂ enabling near-unity selective photocatalytic CO₂[−] to-methanol conversion. *Nat. Commun.* **2025**, *16*, 7844. [CrossRef] [PubMed]
25. Sun, K.; Guo, X.; Chen, Z.; Gong, X.; Jin, H.; Jin, D. Enhanced photothermal preferential oxidation of CO over TiO₂–MnCo₂O₄@NF catalyst with p-n heterojunction. *Mol. Catal.* **2025**, *587*, 115461. [CrossRef]
26. Pu, B.; Tuersun, P.; Li, S.; He, G.; Dou, F.; Lv, S. Light Absorption and Scattering Properties of Ag@TiO₂ Nanosphere Dimer for Photocatalytic Water Purification. *Nanomaterials* **2025**, *15*, 1618. [CrossRef]
27. Jin, R.; Li, R.; Ma, M.L.; Chen, D.Y.; Zhang, J.Y.; Xie, Z.H.; Ding, L.F.; Xie, Y.; Li, J.R. Beyond Tradition: A MOF-On-MOF Cascade Z-Scheme Heterostructure for Augmented CO₂ Photoreduction. *Small* **2025**, e2409759. [CrossRef]
28. Zhang, D.; Gu, H.; Liu, X.-H.; Kong, Q. Constructed pyrene-based Zn-MOF/carbon nitride heterojunction for efficient CO₂ Photoreduction to CH₄. *Inorg. Chem. Commun.* **2026**, *185*, 116072. [CrossRef]
29. Liu, L.; Zhang, L.; Du, X.; Li, P.; Wang, R.; Deng, Y.; An, X.; Wu, X. Boosting electron transfer in Lewis-acid MOF facilitates photoreduction of CO₂ to ethanol. *Appl. Catal. B Environ. Energy* **2026**, *384*, 126183. [CrossRef]
30. Shi, J.; Ju, C.; Yang, T.; Shi, J.; Pu, K.; Zhao, T.; Zheng, N.; Nie, L.; Xue, K.; Gao, Y. Carbon quantum dots modified NH₂[−] MIL-125(Ti) acid-etching derived TiO₂[−]-based photocatalysts and efficient removal of high concentrations of dyes from wastewater under visible light. *Colloids Surf. A Physicochem. Eng. Asp.* **2023**, *677*, 132378. [CrossRef]
31. Yang, X.; Lan, X.; Zhang, Y.; Li, H.; Bai, G. Rational design of MoS₂@COF hybrid composites promoting C-C coupling for photocatalytic CO₂ reduction to ethane. *Appl. Catal. B Environ.* **2023**, *325*, 122393. [CrossRef]
32. Wang, M.; Li, Y.; Li, R.; Zhang, Y.; Yue, D.; Zhao, S.; Chen, M.; Song, H. In Situ Construction of 2D/2D g-C₃N₄/rGO Hybrid Photocatalysts for Efficient Ciprofloxacin Degradation. *Nanomaterials* **2025**, *15*, 1641. [CrossRef] [PubMed]
33. Kaur, A.; Kansal, S.K. Flower shaped Bi₂O_{2.33}/Bi₂WO₆ composite: An efficient photocatalyst for degradation of methylene blue from aqueous solution in direct solar light. *Chemosphere* **2023**, *11*, 140862. [CrossRef] [PubMed]
34. Wen, X.J.; Wu, X.; Hu, L.; Wu, X.K.; Guo, H.; Qian, B.B.; Liu, Z.T.; Li, H.Z.; Fei, Z.H. A critical review on modification strategies of Bi₂Sn₂O₇ photocatalysts and their applications in energy and environmental remediation fields. *Coord. Chem. Rev.* **2025**, *526*, 216377. [CrossRef]
35. Wang, K.; Sun, T.; Ma, H.; Wang, Y.; He, Z.H.; Wang, H.; Wang, W.; Yang, Y.; Wang, L.; Liu, Z.T. Energy band modulating of NiO/BiOCl heterojunction with transition from type-II to S-scheme for enhancing photocatalytic CO₂ reduction. *Chem. Eng. J.* **2024**, *497*, 154711. [CrossRef]
36. Zhang, J.; Wang, S.; Song, P.; Li, A.; Jiang, W.; Di, J. Copper porphyrin modified BiOBr/Bi₁₉S₂₇Br₃ for efficient CO₂ photoreduction. *J. Colloid Interface Sci.* **2024**, *679*, 383–390. [CrossRef]
37. Ding, X.; Jing, W.; Bai, S.; Kang, X.; Yu, F.; Ma, T.; Wang, F.; Liu, Y.; Guo, L. Infrared light promotes reverse hydrogen spillover for boosting photoconversion of CO₂ to CH₄ on Bi/BVOv. *Chem. Eng. J.* **2025**, *523*, 168447. [CrossRef]

38. Tan, C.; Ai, L.; Wang, L.; Jia, D.; Guo, N.; Zha, M. Revealing the nature of asymmetric Lewis acid sites by dual-orbital hybridization in $\text{Tb-BiO}_{1-x}\text{Cl}/\text{BiO}_{1-x}\text{Cl}$ homostructure for superior photocatalytic performance. *Appl. Catal. B Environ. Energy* **2025**, *373*, 125336. [CrossRef]
39. Li, M.; Huang, H.; Yu, S.; Tian, N.; Zhang, Y. Facet, Junction and Electric Field Engineering of Bismuth-Based Materials for Photocatalysis. *ChemCatChem* **2018**, *10*, 4477–4496. [CrossRef]
40. Zhang, L.; Yang, J.; Zhao, X.; Xiao, X.; Sun, F.; Zuo, X.; Nan, J. Small-molecule surface-modified bismuth-based semiconductors as a new class of visible-light-driven photocatalytic materials: Structure-dependent photocatalytic properties and photosensitization mechanism. *Chem. Eng. J.* **2020**, *380*, 122546. [CrossRef]
41. Xu, M.; Yang, J.; Sun, C.; Liu, L.; Cui, Y.; Liang, B. Performance enhancement strategies of bi-based photocatalysts: A review on recent progress. *Chem. Eng. J.* **2020**, *389*, 124402. [CrossRef]
42. Dhakshinamoorthy, A.; Navalon, S.; Corma, A.; Garcia, H. Photocatalytic CO_2 reduction by TiO_2 and related titanium containing solids. *Energy Environ. Sci.* **2012**, *5*, 9217–9233. [CrossRef]
43. Li, R.; Zhang, W.; Zhou, K. Metal–Organic-Framework-Based Catalysts for Photoreduction of CO_2 . *Adv. Mater.* **2018**, *30*, 1705512. [CrossRef] [PubMed]
44. Yang, M.-Q.; Xu, Y.-J. Photocatalytic conversion of CO_2 over graphene-based composites: Current status and future perspective. *Nanoscale Horiz.* **2016**, *1*, 231–254. [CrossRef]
45. Xu, X.; Ding, X.; Yang, X.; Wang, P.; Li, S.; Lu, Z.; Chen, H. Oxygen vacancy boosted photocatalytic decomposition of ciprofloxacin over Bi_2MoO_6 : Oxygen vacancy engineering, biotoxicity evaluation and mechanism study. *J. Hazard. Mater.* **2019**, *364*, 691–699. [CrossRef]
46. Kumar, B.; Llorente, M.; Froehlich, J.; Dang, T.; Sathrum, A.; Kubiak, C.P. Photochemical and photoelectrochemical reduction of CO_2 . *Annu. Rev. Phys. Chem.* **2012**, *63*, 541–569. [CrossRef]
47. Wang, W.H.; Himeda, Y.; Muckerman, J.T.; Manbeck, G.F.; Fujita, E. CO_2 Hydrogenation to Formate and Methanol as an Alternative to Photo- and Electrochemical CO_2 Reduction. *Chem. Rev.* **2015**, *115*, 12936–12973. [CrossRef]
48. Thompson, W.A.; Sanchez Fernandez, E.; Maroto-Valer, M.M. Probability Langmuir-Hinshelwood based CO_2 photoreduction kinetic models. *Chem. Eng. J.* **2020**, *384*, 123356. [CrossRef]
49. Liang, L.; Li, X.; Sun, Y.; Tan, Y.; Jiao, X.; Ju, H.; Qi, Z.; Zhu, J.; Xie, Y. Infrared Light-Driven CO_2 Overall Splitting at Room Temperature. *Joule* **2018**, *2*, 1004–1016. [CrossRef]
50. Rej, S.; Bisetto, M.; Naldoni, A.; Fornasiero, P. Well-defined Cu_2O photocatalysts for solar fuels and chemicals. *J. Mater. Chem. A* **2021**, *9*, 5915–5951. [CrossRef]
51. Tu, W.; Zhou, Y.; Zou, Z. Photocatalytic conversion of CO_2 into renewable hydrocarbon fuels: State-of-the-art accomplishment, challenges, and prospects. *Adv. Mater.* **2014**, *26*, 4607–4626. [CrossRef] [PubMed]
52. Chang, X.; Wang, T.; Gong, J. CO_2 photo-reduction: Insights into CO_2 activation and reaction on surfaces of photocatalysts. *Energy Environ. Sci.* **2016**, *9*, 2373–2385. [CrossRef]
53. Li, X.; Yu, J.; Jaroniec, M.; Chen, X. Cocatalysts for Selective Photoreduction of CO_2 into Solar Fuels. *Chem. Rev.* **2019**, *119*, 3962–4179. [CrossRef] [PubMed]
54. Nakada, A.; Koike, K.; Maeda, K.; Ishitani, O. Highly efficient visible-light-driven CO_2 reduction to CO using a $\text{Ru(II)}\text{--Re(I)}$ supramolecular photocatalyst in an aqueous solution. *Green Chem.* **2016**, *18*, 139–155. [CrossRef]
55. Li, Y.; Wang, W.-N.; Zhan, Z.; Woo, M.-H.; Wu, C.-Y.; Biswas, P. Photocatalytic reduction of CO_2 with H_2O on mesoporous silica supported Cu/TiO_2 catalysts. *Appl. Catal. B Environ.* **2010**, *100*, 386–392. [CrossRef]
56. Sorcar, S.; Yoriya, S.; Lee, H.; Grimes, C.A.; Feng, S.P. A review of recent progress in gas phase CO_2 reduction and suggestions on future advancement. *Mater. Today* **2020**, *16*, 100264. [CrossRef]
57. Kong, T.; Jiang, Y.; Xiong, Y. Photocatalytic CO_2 conversion: What can we learn from conventional CO_x hydrogenation? *Chem. Soc. Rev.* **2020**, *49*, 6579–6591. [CrossRef]
58. Sorcar, S.; Thompson, J.; Hwang, Y.; Park, Y.H.; Majima, T.; Grimes, C.A.; Durrant, J.R.; In, S.-I. High-rate solar-light photoconversion of CO_2 to fuel: Controllable transformation from C_1 to C_2 products. *Energy Environ. Sci.* **2018**, *11*, 3183–3193. [CrossRef]
59. Habisreutinger, S.N.; Schmidt-Mende, L.; Stolarczyk, J.K. Photocatalytic Reduction of CO_2 on TiO_2 and Other Semiconductors. *Angew. Chem.* **2013**, *52*, 7372–7408. [CrossRef]
60. Ji, Y.; Luo, Y. Theoretical Study on the Mechanism of Photoreduction of CO_2 to CH_4 on the Anatase $\text{TiO}_2(101)$ Surface. *ACS Catal.* **2016**, *6*, 2018–2025. [CrossRef]
61. Ong, W.J.; Putri, L.K.; Mohamed, A.R. Rational Design of Carbon-Based 2D Nanostructures for Enhanced Photocatalytic CO_2 Reduction: A Dimensionality Perspective. *Chem. Eur. J.* **2020**, *26*, 9710–9748. [CrossRef]
62. Wei, T.; Xiao, H.; Niu, R.; Xu, B.; Li, H.; Yan, X.; Li, Y.; Ou, H.; Lin, B.; Yang, G. Dual plasmonic coupling effect in Bi/vacancy-rich Bi_2WO_6 heterojunction for selective CO_2 photoreduction to CH_4 . *Chem. Eng. Sci.* **2024**, *292*, 120012. [CrossRef]

63. Ai, Z.; Yu, H.; Lee, S.; Zhang, L. Monoclinic α - Bi_2O_3 photocatalyst for efficient removal of gaseous NO and HCHO under visible light irradiation. *J. Alloys Compd.* **2011**, *509*, 2044–2049. [[CrossRef](#)]
64. Komatsu, T.; Dimitrov, V.; Tasheva, T.; Honma, T. A review: A new insight for electronic polarizability and chemical bond strength in Bi_2O_3 -based glasses. *J. Non-Cryst. Solids* **2020**, *550*, 120365. [[CrossRef](#)]
65. Hajibigloo, L.; Zhiani, R.; Hosseiny, M.; Moghaddam, H.H.; Ebrahimi, Z. Enhanced photohydrogenation of carbon dioxide to methane using $\text{Bi}_2\text{Sn}_2\text{O}_7/\text{Bi}_2\text{O}_3$. *Inorg. Chem. Commun.* **2025**, *177*, 114375. [[CrossRef](#)]
66. Abdi, F.F.; Savenije, T.J.; May, M.M.; Dam, B.; Roel, V. The Origin of Slow Carrier Transport in BiVO_4 Thin Film Photoanodes: A Time-Resolved Microwave Conductivity Study. *J. Phys. Chem. Lett.* **2013**, *4*, 2752–2757. [[CrossRef](#)]
67. Malathi, A.; Madhavan, J.; Ashokkumar, M.; Arunachalam, P. A review on BiVO_4 photocatalyst: Activity enhancement methods for solar photocatalytic applications. *Appl. Catal. A* **2018**, *555*, 47–74.
68. Liu, X.; Gu, S.; Zhao, Y.; Zhou, G.; Li, W. BiVO_4 , Bi_2WO_6 and Bi_2MoO_6 photocatalysis: A brief review. *J. Mater. Sci. Technol.* **2020**, *56*, 45–65. [[CrossRef](#)]
69. He, H.; Jiao, Y.; Li, Y.P.; Ying, Z.; Wang, C. Size controllable synthesis of single-crystal ferroelectric $\text{Bi}_4\text{Ti}_3\text{O}_{12}$ nanosheet dominated with {001} facets toward enhanced visible-light-driven photocatalytic activities. *Appl. Catal. B Environ.* **2014**, *156–157*, 35–43. [[CrossRef](#)]
70. Pérez, S.; Vázquez-García, A.; Gutiérrez-Pérez, A.; Ayala-Ayala, M.T.; Boujnah, M.; Tapia-P, J.; Díaz-Real, J.A.; Muñoz-Saldaña, J. Boosting visible light-driven photocatalysis with bismuth titanate ($\text{Bi}_2\text{Ti}_4\text{O}_{11}/\text{Bi}_4\text{Ti}_3\text{O}_{12}$) heterojunctions. *Environ. Res.* **2026**, *289*, 123384. [[CrossRef](#)]
71. Visible-light photocatalysis with bismuth titanate ($\text{Bi}_{12}\text{TiO}_{20}$) particles synthesized by the oxidant peroxide method (OPM). *Ceram. Int.* **2015**, *41*, 12073–12080. [[CrossRef](#)]
72. Huang, J.Y.; Zhang, K.Q.; Lai, Y.K. Fabrication, Modification, and Emerging Applications of TiO_2 Nanotube Arrays by Electrochemical Synthesis: A Review. *Int. J. Photoenergy* **2013**, *112*, 4696–4701.
73. Yan, Z.; Fang, D.; Chen, M.; Yi, X. Synthetic $\text{Bi}_2\text{O}_2\text{CO}_3$ nanostructures: Novel photocatalyst with controlled special surface exposed. *Mol. Catal.* **2010**, *317*, 34–40.
74. Huang, S.; Shen, J.; Wu, Y.; Li, X.; Ma, Y.; Xie, Y.; Yu, C.; Zhang, Y.; Zhang, J. $\text{Bi}_2\text{O}_2\text{CO}_3$ co-catalyst modification BiOBr driving efficient photoreduction CO_2 . *Colloids Surf. A Physicochem. Eng. Asp.* **2025**, *725*, 137731. [[CrossRef](#)]
75. Zhang, L.; Zhu, Y. A review of controllable synthesis and enhancement of performances of bismuth tungstate visible-light-driven photocatalysts. *Catal. Sci. Technol.* **2012**, *2*, 694. [[CrossRef](#)]
76. Zhu, Y.; Liu, Y.; Lv, Y.; Qiang, L.; Di, L.; Zhu, Y. Enhancement of photocatalytic activity for BiPO_4 via phase junction. *J Mater Chem A* **2014**, *2*, 13041–13048. [[CrossRef](#)]
77. Arnold, D.C. Composition-driven structural phase transitions in rare-earth-doped bifeo3 ceramics: A review. *IEEE Trans. Ultrason. Ferroelectr. Freq. Control* **2015**, *62*, 62–82. [[CrossRef](#)]
78. Cheng, H.; Huang, B.; Dai, Y. Engineering BiOX ($X = \text{Cl}, \text{Br}, \text{I}$) nanostructures for highly efficient photocatalytic applications. *Nanoscale* **2014**, *6*, 2009–2026. [[CrossRef](#)]
79. Garg, S.; Yadav, M.; Chandra, A.; Hernadi, K. A Review on BiOX ($X = \text{Cl}, \text{Br}$ and I) Nano-/Microstructures for Their Photocatalytic Applications. *J. Nanosci. Nanotechnol.* **2019**, *19*, 280–294. [[CrossRef](#)]
80. Liu, Q.; Bai, C.; He, D.; Wu, X.; Wu, Y.; Chen, R. Oxygen vacancy mediation of BiOX ($X = \text{Cl}, \text{Br}$) towards enhanced photocatalytic CO_2 reduction activity. *J. Environ. Chem. Eng.* **2024**, *12*, 112449. [[CrossRef](#)]
81. Xu, L.; Wan, Y.; Xie, H.; Huang, Y.; Qiao, X.; Qin, L.; Seo, H.J. On Structure, Optical Properties and Photodegraded Ability of Aurivillius-Type $\text{Bi}_3\text{TiNbO}_9$ Nanoparticles. *J. Am. Ceram. Soc.* **2016**, *99*, 3964–3972. [[CrossRef](#)]
82. Bac, L.H.; Le, T.; Chinh, N.V.; Khoa, N.T.; Thiet, D.V.; Trung, T.V.; Dang, D.D. Tailoring the structural, optical properties and photocatalytic behavior of ferroelectric $\text{Bi}_{0.5}\text{K}_{0.5}\text{TiO}_3$ nanopowders. *Mater. Lett.* **2016**, *164*, 631–635. [[CrossRef](#)]
83. Xiao, X.; Hu, R.; Liu, C.; Xing, C.; Qian, C.; Zuo, X.; Nan, J.; Wang, L. Facile large-scale synthesis of β - Bi_2O_3 nanospheres as a highly efficient photocatalyst for the degradation of acetaminophen under visible light irradiation. *Appl. Catal. B Environ.* **2013**, *140–141*, 433–443. [[CrossRef](#)]
84. Díaz-Guerra, C.; Almodóvar, P.; Camacho-López, M.; Camacho-López, S.; Piqueras, J. Formation of β - Bi_2O_3 and δ - Bi_2O_3 during laser irradiation of Bi films studied in-situ by spatially resolved Raman spectroscopy. *J. Alloys Compd.* **2017**, *723*, 108–118. [[CrossRef](#)]
85. Wang, J.; Yang, X.; Zhao, K. Precursor-induced fabrication of β - Bi_2O_3 microspheres and their performance as visible-light-driven photocatalysts. *J. Mater. Chem. A* **2013**, *1*, 9069–9074. [[CrossRef](#)]
86. Chen, X.; Zhang, Z.; Chi, L.; Nair, A.K.; Shangguan, W.; Jiang, Z. Recent Advances in Visible-Light-Driven Photoelectrochemical Water Splitting: Catalyst Nanostructures and Reaction Systems. *Nano-Micro Lett.* **2016**, *8*, 1–12. [[CrossRef](#)]
87. Tan, C.; Ai, L.; Sheng, R.; Wang, L.; Guo, N.; Xu, M.; Jia, D. Delocalization of Bi^{3+} ions in BiOCl induced by Bi-S bonds for highly selective photoreduction of CO_2 to CO. *Sep. Purif. Technol.* **2025**, *363*, 132049. [[CrossRef](#)]

88. Kim, J.; Do, J.Y.; Park, N.-K.; Lee, S.J.; Hong, J.-P.; Kang, M. Photoreduction of CO₂ into CH₄ using Bi₂S₃-TiO₂ double-layered dense films. *Korean J. Chem. Eng.* **2025**, *35*, 1089–1098. [\[CrossRef\]](#)
89. Yu, C.; Wang, K.; Yang, P.; Yang, S.; Lu, C.; Song, Y.; Dong, S.; Sun, J.; Sun, J. One-pot facile synthesis of Bi₂S₃/SnS₂/Bi₂O₃ ternary heterojunction as advanced double Z-scheme photocatalytic system for efficient dye removal under sunlight irradiation. *Appl. Surf. Sci.* **2017**, *420*, 233–242.
90. Ai, L.; Wang, L.; Xu, M.; Zhang, S.; Jia, L. Defective Bi₃₃₃(Bi₆S₉)Br/Bi₂S₃ heterostructure nanorods: Boosting the activity for efficient visible-light photocatalytic Cr(VI) reduction. *Appl. Catal. B Environ.* **2021**, *284*, 119730. [\[CrossRef\]](#)
91. Xiang, J.; Li, X.; Mo, R.; Liu, Y.; Li, H. Seed layer-assisted growth of branched Bi₂S₃ nanostructure on α-Fe₂O₃ thin film for improved photoelectrochemical performance. *J. Mater. Sci. Mater. Electron.* **2021**, *32*, 13040–13050. [\[CrossRef\]](#)
92. Xin, L.; Chen, J.; Li, H.; Li, J. Photoreduction of CO₂ to methanol over Bi₂S₃/CdS photocatalyst under visible light irradiation. *J. Nat. Gas Chem.* **2011**, *20*, 413–417.
93. McDowell, N.A.; Knight, K.S.; Lightfoot, P. Unusual high-temperature structural behaviour in ferroelectric Bi₂WO₆. *Green Chem.* **2010**, *37*, 11–18. [\[CrossRef\]](#) [\[PubMed\]](#)
94. Lin, J.; He, J.; Huang, Q.; Luo, Y.; Zhang, Y.; Li, W.; Zhou, G.; Hu, J.; Yang, Z.; Zhou, Y. Interfacial Bi-O-C bonds and rich oxygen vacancies synergistically endow carbon quantum dot/Bi₂MoO₆ with prominent photocatalytic CO₂ reduction into CO. *Appl. Catal. B Environ. Energy* **2024**, *362*, 127747. [\[CrossRef\]](#)
95. Chengula, P.J.; Charles, H.; Seo, J.Y.; Lee, C.S. Ascorbic Acid-Assisted Morphology Tailoring of Crystalline Bi₂WO₆ for the Application in CO₂ Photoreduction. *Int. J. Precis. Eng. Manuf. Green Technol.* **2025**, *12*, 1277–1294. [\[CrossRef\]](#)
96. Sun, S.; Wang, W. Advanced chemical compositions and nanoarchitectures of bismuth based complex oxides for solar photocatalytic application. *RSC Adv.* **2014**, *4*, 47136–47152. [\[CrossRef\]](#)
97. Tuerhong, R.; Zhang, P.; Zhang, Y.; Lan, Y.; Chai, K.; Su, X.; Han, L.; Wang, X.; Han, Y. Cation vacancy engineering: Electronic structure reconstruction in Bi₂WO₆ facilitates CO₂ photoreduction. *J. Alloys Compd.* **2025**, *1047*, 184969. [\[CrossRef\]](#)
98. Jing, T.; Dai, Y.; Wei, W.; Ma, X.; Huang, B. Near-infrared photocatalytic activity induced by intrinsic defects in Bi₂MO₆ (M = W, Mo). *Phys. Chem. Chem. Phys.* **2014**, *16*, 18596–18604. [\[CrossRef\]](#)
99. Collado, L.; Gomez-Mendoza, M.; García-Tecedor, M.; Oropeza, F.E.; Reynal, A.; Durrant, J.R.; Serrano, D.P.; de la Peña O'Shea, V.A. Towards the improvement of methane production in CO₂ photoreduction using Bi₂WO₆/TiO₂ heterostructures. *Appl. Catal. B Environ. Energy* **2022**, *324*, 122206. [\[CrossRef\]](#)
100. Zhang, Y.; Liu, S.; Guo, X.; Mikulfcifá, H.; Xiao, R.; Wang, X. F,ai doped Bi₂MoO₆ nanosheets for photoreduction of CO₂ with H₂O. *J. Photochem. Photobiol. A Chem.* **2023**, *447*, 115278. [\[CrossRef\]](#)
101. Lai, K.; Wei, W.; Zhu, Y.; Guo, M.; Dai, Y.; Huang, B. Effects of oxygen vacancy and N-doping on the electronic and photocatalytic properties of Bi₂MO₆ (M=Mo, W). *J. Solid State Chem.* **2012**, *187*, 103–108.
102. Liu, J.; Liu, X.; Dai, C.; Zeng, C.; Ali, S.; Bououdina, M.; Jia, Y. Copper-doped Bi₂MoO₆ with concurrent oxygen vacancies for enhanced CO₂ photoreduction. *Inorg. Chem. Front.* **2024**, *11*, 8003–8015. [\[CrossRef\]](#)
103. Niu, L.; Liu, X.; Liu, X.; Yu, J.; Chen, R.; Yang, K.; Chen, L.; Hu, M.; Wu, J.; Hosseini-Bandegharai, A. Constructing a 3D Bi₂WO₆/Cd_{0.3}Zn_{0.7}S heterojunction to enhance photocatalytic CO₂ reduction efficiency. *J. Environ. Chem. Eng.* **2026**, *14*, 121167. [\[CrossRef\]](#)
104. Yuan, S.; Zhao, Y.; Chen, W.; Wu, C.; Wang, X. Self-Assembled 3D Hierarchical Porous Bi₂MoO₆ Microspheres toward High Capacity and Ultra-Long-Life Anode Material for Li-Ion Batteries. *ACS Appl. Mater. Interfaces* **2017**, *9*, 22695–22706. [\[CrossRef\]](#) [\[PubMed\]](#)
105. Chen, T.; Liu, L.; Hu, C.; Huang, H. Recent advances on Bi₂WO₆-based photocatalysts for environmental and energy applications. *Chin. J. Catal.* **2021**, *42*, 1413–1438. [\[CrossRef\]](#)
106. Jiang, Z.; Liang, X.; Zheng, H.; Liu, Y.; Wang, Z.; Wang, P.; Zhang, X.; Qin, X.; Dai, Y.; Whangbo, M.-H.; et al. Photocatalytic reduction of CO₂ to methanol by three-dimensional hollow structures of Bi₂WO₆ quantum dots. *Appl. Catal. B Environ.* **2017**, *219*, 209–215. [\[CrossRef\]](#)
107. Wang, T.; Feng, C.; Liu, J.; Wang, D.; Hu, H.; Hu, J.; Chen, Z.; Xue, G. Bi₂WO₆ hollow microspheres with high specific surface area and oxygen vacancies for efficient photocatalysis N₂ fixation. *Chem. Eng. J.* **2021**, *414*, 128827. [\[CrossRef\]](#)
108. Etogo, A.; Liu, R.; Ren, J.; Qi, L.; Zheng, C.; Ning, J.; Zhong, Y.; Hu, Y. Facile one-pot solvothermal preparation of Mo-doped Bi₂WO₆ biscuit-like microstructures for visible-light-driven photocatalytic water oxidation. *J. Mater. Chem. A* **2016**, *4*, 13242–13250. [\[CrossRef\]](#)
109. Tokunaga, S.; Kato, H.; Kudo, A. Selective Preparation of Monoclinic and Tetragonal BiVO₄ with Scheelite Structure and Their Photocatalytic Properties. *ChemInform* **2002**, *33*, 111–121. [\[CrossRef\]](#)
110. Zhao, Z.; Li, Z.; Zou, Z. Electronic structure and optical properties of monoclinic clinobisvanite BiVO₄. *Phys. Chem. Chem. Phys.* **2011**, *13*, 4746–4753. [\[CrossRef\]](#)
111. Gong, S.; Rao, F.; Zhang, W.; Hassan, Q.-U.; Liu, Z.; Gao, J.; Lu, J.; Hojamberdiev, M.; Zhu, G. Au nanoparticles loaded on hollow BiOCl microstructures boosting CO₂ photoreduction. *Chin. Chem. Lett.* **2021**, *33*, 4385–4388. [\[CrossRef\]](#)

112. Shahid, M.Z.; Chen, Z.; Mehmood, R.; Zheng, S.; Idris, A.M.; Li, Z. The synergy of active sites induced by surface pits in BiOCl nanoplates for efficient CO₂ photoreduction. *Mater. Today* **2023**, *34*, 101303. [\[CrossRef\]](#)
113. Ma, S.; Yang, P.; Sun, H.; Guo, R.; Wang, Z.; Li, Q.; Luo, X.; Li, X. Enhanced CO₂ photoreduction by constructing BiOCl/NiS Schottky heterojunction with a giant internal electric field. *Sep. Purif. Technol.* **2024**, *354*, 128976. [\[CrossRef\]](#)
114. Cui, P.; Wang, J.; Wang, Z.; Chen, J.; Xing, X.; Wang, L.; Yu, R. Bismuth oxychloride hollow microspheres with high visible light photocatalytic activity. *Nano Res.* **2016**, *9*, 593–601. [\[CrossRef\]](#)
115. Tan, C.; Ai, L.; Wang, L.; Xu, M.; Guo, N.; Jia, D. Selective CO production via a dual-defective CdS/BiOCl photocatalyst for CO₂ photoreduction. *J. Mater. Chem. A* **2024**, *12*, 25371–25380. [\[CrossRef\]](#)
116. Ding, C.; Ma, Z.; Han, C.; Liu, X.; Jia, Z.; Xie, H.; Bao, K.; Ye, L. Large-scale preparation of BiOX (X = Cl, Br) ultrathin nanosheets for efficient photocatalytic CO₂ conversion. *J. Taiwan Inst. Chem. Eng.* **2017**, *78*, 395–400. [\[CrossRef\]](#)
117. Zhao, L.; Hou, H.; Wang, S.; Wang, L.; Yang, Y.; Bowen, C.R.; Wang, J.; Liao, Z.; Yang, D.; Yan, R.; et al. Engineering Co Single Atoms in Ultrathin BiOCl Nanosheets for Boosted CO₂ Photoreduction. *Adv. Funct. Mater.* **2024**, *35*, 202416346. [\[CrossRef\]](#)
118. Wu, D.; Liu, D.; Luo, H.; Wang, J.; Dong, Y. Atomic-scale frustrated Lewis pairs in ultrathin BiOCl nanosheets: Dynamic oxygen vacancy engineering for efficient CO₂ photoreduction. *Chem. Eng. J.* **2025**, *522*, 167514. [\[CrossRef\]](#)
119. Fabiano, B.; Reverberi, A.P.; Varbanov, P.S. Safety opportunities for the synthesis of metal nanoparticles and short-cut approach to workplace risk evaluation. *J. Clean. Prod.* **2019**, *209*, 297–308. [\[CrossRef\]](#)
120. Cao, J.; Cao, B.; Wang, Z.; Jing, B.; Li, R.; Wang, J. Synergistically enhancing CO₂ photoreduction over BiOBr nanosheets via Ce doping and induced oxygen vacancy. *J. Alloys Compd.* **2025**, *1036*, 182064. [\[CrossRef\]](#)
121. You, R.-J.; Wang, K.; Ma, H.; Li, X.-P.; Cao, Z.; He, Z.-H.; Wang, H.; Wang, W.; Lai, X.; Liu, Z.-T. Co species modulating of BiOBr-based Z-scheme heterojunction for the transform photoreduction CO₂ products from CO to CH₄. *Chem. Eng. J.* **2025**, *510*, 161754. [\[CrossRef\]](#)
122. Peng, T.; Wang, Y.; Wang, K.; Zhang, K.; Wang, Y.; Xu, Y.; Guan, Q.; Wang, G.; Zhang, W.; Wu, B.; et al. Atomically dispersed Co sites on BiOCl nanosheets for efficient CO₂ photoreduction. *Green Energy Environ.* **2025**, *10*, 1948–1955. [\[CrossRef\]](#)
123. Liu, J.; Qin, W.; Wang, Y.; Xu, Q.; Xie, Y.; Chen, Y.; Dai, Y.; Zhang, W. NH₂-UiO-66 modification BiOBr enhancement photoreduction CO₂ to CO. *Sep. Purif. Technol.* **2024**, *344*, 127289. [\[CrossRef\]](#)
124. Wang, Z.; Cao, B.; Li, R.; Jing, B.; Cai, X.; Cao, J.; He, D.; Xu, Y. Constructing 2D/2D BiOI/Bi₂O₂CO₃ S-scheme heterojunction for boosted CO₂ photoreduction. *J. Alloys Compd.* **2025**, *1037*, 182207. [\[CrossRef\]](#)
125. Wei, J.; Dong, H.; Gao, Y.; Su, X.; Tan, H.; Li, J.; Zhao, Q.; Guan, X.; Lu, Z.; Ouyang, J.; et al. Synergism of oxygen, Iodine binary vacancies with the interfacial electric field: Enhancing CO₂ photoreduction over BiVO₄-BiOCl/BiOI atomic-thin nanosheets. *J. Mater. Chem. A* **2023**, *11*, 4057–4066. [\[CrossRef\]](#)
126. Nie, J.; Zhang, X.; Wang, M.; Ou, Y.; Li, S.; Zhong, P.; Wang, W.; Zhu, G.; Ma, X. MXene quantum dots decorated g-C₃N₄/BiOI heterojunction photocatalyst for efficient NO deep oxidation and CO₂ reduction. *Sep. Purif. Technol.* **2024**, *354*, 128961. [\[CrossRef\]](#)
127. Yang, C.; Zhang, Q.; Wang, W.; Cheng, B.; Yu, J.; Cao, S. 2D/2D g-C₃N₄@BiOI S-scheme heterojunction with gas-liquid-solid triphase interface for highly efficient CO₂ photoreduction. *Sci. China Mater.* **2024**, *67*, 1830–1838. [\[CrossRef\]](#)
128. Zhu, S.; Li, X.; Jiao, X.; Shao, W.; Li, L.; Zu, X.; Hu, J.; Zhu, J.; Yan, W.; Wang, C.; et al. Selective CO(2) Photoreduction into C(2) Product Enabled by Charge-Polarized Metal Pair Sites. *Nano Lett.* **2021**, *21*, 2324–2331. [\[CrossRef\]](#)
129. Chang, C.-C.; Li, E.Y.; Tsai, M.-K. A computational exploration of CO₂ reduction via CO dimerization on mixed-valence copper oxide surface. *Phys. Chem. Chem. Phys.* **2018**, *20*, 16675–16683. [\[CrossRef\]](#)
130. Kumar, A.; Singh, P.; Khan, A.A.P.; Le, Q.V.; Nguyen, V.-H.; Thakur, S.; Raizada, P. CO₂ photoreduction into solar fuels via vacancy engineered bismuth-based photocatalysts: Selectivity and mechanistic insights. *Chem. Eng. J.* **2022**, *439*, 135563. [\[CrossRef\]](#)
131. Li, X.; Sun, Y.; Xu, J.; Shao, Y.; Wu, J.; Xu, X.; Pan, Y.; Ju, H.; Zhu, J.; Xie, Y. Selective visible-light-driven photocatalytic CO₂ reduction to CH₄ mediated by atomically thin CuIn₅S₈ layers. *Nature* **2019**, *4*, 690–699. [\[CrossRef\]](#)
132. Ji, Y.; Luo, Y. Direct Donation of Protons from H₂O to CO₂ in Artificial Photosynthesis on the Anatase TiO₂(101) Surface. *J. Phys. Chem. C* **2019**, *123*, 3019–3023. [\[CrossRef\]](#)
133. Zhang, L.; Wang, W.; Jiang, D.; Gao, E.; Sun, S. Photoreduction of CO₂ on BiOCl nanoplates with the assistance of photoinduced oxygen vacancies. *Nano Res.* **2015**, *8*, 821–831. [\[CrossRef\]](#)
134. Di, J.; Zhu, C.; Ji, M.; Duan, M.; Long, R.; Yan, C.; Gu, K.; Xiong, J.; She, Y.; Xia, J.; et al. Defect-Rich Bi₁₂O₁₇Cl₂ Nanotubes Self-Accelerating Charge Separation for Boosting Photocatalytic CO₂ Reduction. *Angew. Chem. Int. Ed.* **2018**, *57*, 14847–14851. [\[CrossRef\]](#) [\[PubMed\]](#)
135. Wang, B.; Yang, S.-Z.; Chen, H.; Gao, Q.; Weng, Y.-X.; Zhu, W.; Liu, G.; Zhang, Y.; Ye, Y.; Zhu, H.; et al. Revealing the role of oxygen vacancies in bimetallic PbBiO₂Br atomic layers for boosting photocatalytic CO₂ conversion. *Appl. Catal. B Environ.* **2020**, *277*, 119170. [\[CrossRef\]](#)
136. Guo, S.; Di, J.; Chen, C.; Zhu, C.; Duan, M.; Lian, C.; Ji, M.; Zhou, W.; Xu, M.; Song, P.; et al. Oxygen vacancy mediated bismuth stannate ultra-small nanoparticle towards photocatalytic CO₂ to CO conversion. *Appl. Catal. B Environ.* **2020**, *276*, 119156. [\[CrossRef\]](#)

137. Xin, Y.K.; Choo, Y.Y.; Chai, S.P.; Ai, K.S.; Mohamed, A.R. Oxygen vacancies induced Bi₂WO₆ for realization of full solar spectrum photocatalytic CO₂ reduction: From UV to NIR region. *Chem. Commun.* **2016**, *52*, 14242–14245.
138. Highly Efficient and Exceptionally Durable CO₂ Photoreduction to Methanol over Freestanding Defective Single-unit-cell Bismuth Vanadate Layers. *J. Am. Chem. Soc.* **2017**, *139*, 3438. [\[CrossRef\]](#)
139. Shan, G.; Jiao, X.; Sun, Z.; Zhang, W.; Xie, Y. Ultrathin Co₃O₄ Layers Realizing Optimized CO₂ Electroreduction to Formate. *Angew. Chem.* **2016**, *55*, 698–702.
140. Liang, L.; Lei, F.; Gao, S.; Sun, Y.; Jiao, X.; Wu, J. Single Unit Cell Bismuth Tungstate Layers Realizing Robust Solar CO₂ Reduction to Methanol. *Angew. Chem.* **2015**, *54*, 2155–2159. [\[CrossRef\]](#)
141. Zhao, M.; Qin, J.; Wang, N.; Zhang, Y.; Cui, H. Reconstruction of surface oxygen vacancy for boosting CO₂ photoreduction mediated by BiOBr/CdS heterojunction. *Sep. Purif. Technol.* **2023**, *329*, 125179. [\[CrossRef\]](#)
142. Wang, Y.; Luo, Y.; Yu, S.; Qin, W.; Xie, Y. Organic-inorganic hybridization strategy for promoting BiOBr CO₂ photoreduction via enhanced CO₂ adsorption and photogenerated carrier migration. *Chin. J. Catal.* **2024**, *429*, 115295. [\[CrossRef\]](#)
143. Ye, L.; Jin, X.; Liu, C.; Ding, C.; Xie, H. Thickness-ultrathin and bismuth-rich strategies for BiOBr to enhance photoreduction of CO₂ into solar fuels. *Appl. Catal. B Environ.* **2016**, *187*, 281–290. [\[CrossRef\]](#)
144. Meng, J.; Duan, Y.; Jing, S.; Ma, J.; Wang, K.; Zhou, K.; Ban, C.; Wang, Y.; Hu, B.; Yu, D.; et al. Facet junction of BiOBr nanosheets boosting spatial charge separation for CO₂ photoreduction. *Nano Energy* **2021**, *92*, 106671. [\[CrossRef\]](#)
145. Lu, Y.; Wu, D.; Qin, Y.; Xie, Y.; Ling, Y.; Ye, H.; Zhang, Y. Facile construction of BiOBr/CoAl-LDH heterojunctions with suppressed Z-axis growth for efficient photoreduction of CO₂. *Sep. Purif. Technol.* **2022**, *302*, 122090. [\[CrossRef\]](#)
146. Zhou, L.; Zhuang, Z.; Zhao, H.; Lin, M.; Zhao, D.; Mai, L. Intricate Hollow Structures: Controlled Synthesis and Applications in Energy Storage and Conversion. *Adv. Mater.* **2017**, *29*, 1602914. [\[CrossRef\]](#)
147. Jin, X.; Lv, C.; Zhou, X.; Xie, H.; Sun, S.; Liu, Y.; Meng, Q.; Chen, G. A bismuth rich hollow Bi₄O₅Br₂ photocatalyst enables dramatic CO₂ reduction activity—ScienceDirect. *Nano Energy* **2025**, *21*, 13–57.
148. Liu, G.; Yu, J.C.; Lu, G.Q.; Cheng, H.M. Crystal facet engineering of semiconductor photocatalysts: Motivations, advances and unique properties. *Chem. Commun.* **2011**, *47*, 6763–6783. [\[CrossRef\]](#)
149. Wang, D.; Jiang, H.; Zong, X.; Xu, Q.; Ma, Y.; Li, G.; Li, C. Crystal Facet Dependence of Water Oxidation on BiVO₄ Sheets under Visible Light Irradiation. *Chem. Eur. J.* **2011**, *17*, 1275–1282. [\[CrossRef\]](#)
150. Wang, S.; Liu, G.; Wang, L. Crystal Facet Engineering of Photoelectrodes for Photoelectrochemical Water Splitting. *Chem. Rev.* **2019**, *119*, 5192–5247. [\[CrossRef\]](#)
151. Wu, D.; Ye, L.; Wong, P.; Keung, Y.; Ho, Y. Organic-free synthesis of {001} facet dominated BiOBr nanosheets for selective photoreduction of CO₂ to CO. *Catal. Sci. Technol.* **2017**, *7*, 265–271. [\[CrossRef\]](#)
152. Ye, L.; Jin, X.; Ji, X.; Liu, C.; Su, Y.; Xie, H.; Liu, C. Facet-dependent photocatalytic reduction of CO₂ on BiOI nanosheets. *Chem. Eng. J.* **2016**, *291*, 39–46. [\[CrossRef\]](#)
153. Chen, F.; Huang, H.; Ye, L.; Zhang, T.; Zhang, Y.; Han, X.; Ma, T. Thickness-Dependent Facet Junction Control of Layered BiOIO₃ Single Crystals for Highly Efficient CO₂ Photoreduction. *Adv. Funct. Mater.* **2018**, *28*, 1804281–1804284. [\[CrossRef\]](#)
154. Wei, Z.-H.; Wang, Y.-F.; Li, Y.-Y.; Zhang, L.; Yao, H.-C. Enhanced photocatalytic CO₂ reduction activity of Z-scheme CdS/BiVO₄ nanocomposite with thinner BiVO₄ nanosheets. *J. CO₂ Util.* **2018**, *28*, 15–25. [\[CrossRef\]](#)
155. Zou, L.; Wang, H.; Wang, X. High Efficient Photodegradation and Photocatalytic Hydrogen Production of CdS/BiVO₄ Heterostructure through Z-scheme Process. *ACS Sustain. Chem. Eng.* **2016**, *5*, 303–309. [\[CrossRef\]](#)
156. He, Y.; Zhang, L.; Fan, M.; Wang, X.; Walbridge, M.L.; Nong, Q.; Wu, Y.; Zhao, L. Z-scheme SnO₂-x/g-C₃N₄ composite as an efficient photocatalyst for dye degradation and photocatalytic CO₂ reduction. *Sol. Energy Mater. Sol. Cells* **2015**, *137*, 175–184. [\[CrossRef\]](#)
157. He, Y.; Zhang, L.; Teng, B.T.; Fan, M. New application of Z-scheme Ag₃PO₄/g-C₃N₄ composite in converting CO₂ to fuel. *Environ. Sci. Technol.* **2015**, *49*, 649–656. [\[CrossRef\]](#)
158. Bai, Y.; Ye, L.; Wang, L.; Shi, X.; Wang, P.; Bai, W.; Wong, P.K. g-C₃N₄/Bi₄O₅I₂ heterojunction with I₃[−]/I[−] redox mediator for enhanced photocatalytic CO₂ conversion. *Appl. Catal. B Environ.* **2016**, *194*, 98–104. [\[CrossRef\]](#)
159. Wang, J.C.; Yao, H.C.; Fan, Z.Y.; Zhang, L.; Wang, J.S. Indirect Z-Scheme BiOI/g-C₃N₄ Photocatalysts with Enhanced Photoreduction CO₂ Activity under Visible Light Irradiation. *ACS Appl. Mater. Interfaces* **2016**, *8*, 3765–3775. [\[CrossRef\]](#)
160. Veisi, H.; Abrifam, M.; Kamangar, S.A.; Pirhayati, M.; Saremi, S.G.; Noroozi, M.; Tamoradi, T.; Karmakar, B. Pd immobilization biguanidine modified Zr-Uio-66 MOF as a reusable heterogeneous catalyst in Suzuki–Miyaura coupling. *Sci. Rep.* **2021**, *11*, 21883. [\[CrossRef\]](#)
161. Li, J.; Shao, W.; Geng, M.; Wan, S.; Ou, M.; Chen, Y. Combined Schottky junction and doping effect in CdxZn1-xS@Au/BiVO₄ Z-Scheme photocatalyst with boosted carriers charge separation for CO₂ reduction by H₂O. *J. Colloid Interface Sci.* **2022**, *606*, 1469–1476. [\[CrossRef\]](#)

162. Lan, Y.; Lu, K.Q.; Fan, Z.; Fu, X.; Xu, Y.J. Unveiling the interplay between light-driven CO₂ photocatalytic reduction and carbonaceous residues decomposition: A case study of Bi₂WO₆-TiO₂ binanosheets. *Appl. Catal. B Environ.* **2018**, *237*, 424–431. [\[CrossRef\]](#)
163. Xiao, Y.; Wu, K.; Gu, S.; Lin, X.; Lin, X.; Zhao, X.; Nan, J.; Zuo, X.; Xiao, X. Cellulose nanocrystal/bismuth/bismuth oxychloride (CNC/Bi/BiOCl) ternary Z-scheme heterojunction with dual oxygen defects and a lowered carboxylic acid intermediate (COOH) formation barrier for efficient visible-light CO₂ photoreduction. *J. Colloid Interface Sci.* **2025**, *694*, 137736. [\[CrossRef\]](#) [\[PubMed\]](#)
164. Hao, L.; Kang, L.; Huang, H.; Ye, L.; Han, K. Surface-Halogenation-Induced Atomic-Site Activation and Local Charge Separation for Superb CO₂ Photoreduction. *Adv. Mater.* **2019**, *31*, e1900546. [\[CrossRef\]](#) [\[PubMed\]](#)
165. Raja, K.S.; Smith, Y.R.; Kondamudi, N.; Manivannan, A.; Misra, M.; Subramanian, V. CO₂ Photoreduction in the Liquid Phase over Pd-Supported on TiO₂ Nanotube and Bismuth Titanate Photocatalysts. *Electrochem. Solid-State Lett.* **2015**, *14*, P1–P4. [\[CrossRef\]](#)
166. Yang, B.; Ye, L.; Li, W.; Xian, S.; Wang, P.; Wei, B. Dual-cocatalysts loading Au/BiOI/MnOx system for enhanced photocatalytic greenhouse gases conversion into solar fuels. *Environ. Sci. Nano* **2016**, *3*, 902–909.
167. Yang, G.; Miao, W.; Yuan, Z.; Jiang, Z.; Huang, B. Bi quantum dots obtained via in situ photodeposition method as a new photocatalytic CO₂ reduction cocatalyst instead of noble metals: Borrowing redox conversion between Bi₂O₃ and Bi. *Appl. Catal. B Environ.* **2018**, *237*, 302–308. [\[CrossRef\]](#)
168. Chen, F.; Ma, Z.; Ye, L.; Ma, T.; Huang, H. Macroscopic Spontaneous Polarization and Surface Oxygen Vacancies Collaboratively Boosting CO₂ Photoreduction on BiOIO₃ Single Crystals. *Adv. Mater.* **2020**, *32*, 1908350. [\[CrossRef\]](#)
169. Li, A.; Hh, A.; Fang, C.A.; Hy, A.; Na, T.A.; Yz, A.; Tzb, C. Cooperation of oxygen vacancies and 2D ultrathin structure promoting CO₂ photoreduction performance of Bi₄Ti₃O₁₂—ScienceDirect. *Sci. Bull.* **2020**, *65*, 934–943.
170. Di, J.; Zhao, X.; Lian, C.; Ji, M.; Xia, J.; Xiong, J. Atomically-thin Bi₂MoO₆ nanosheets with vacancy pairs for improved photocatalytic CO₂ reduction. *Nano Energy* **2019**, *61*, 54–59. [\[CrossRef\]](#)
171. Sun, Y.; Wu, J.; Li, X.; Shi, W.; Ling, P.; Jiao, X.; Gao, S.; Liang, L.; Xu, J.; Yan, W. Efficient Visible-Light-Driven CO₂ Reduction Mediated by Defect-Engineered BiOBr Atomic Layers. *Angew. Chem.* **2018**, *57*, 8719–8723.
172. Qian, Z.; Zhang, L.; Zhang, Y.; Cui, H. Synergistically boosting of CO₂ photoreduction over Bi/BiOBr nanostructure via in-situ formation of oxygen vacancy and metallic Bi. *Sep. Purif. Technol.* **2023**, *324*, 124581. [\[CrossRef\]](#)
173. Di, J.; Chen, C.; Yang, S.-Z.; Chen, S.; Duan, M.; Xiong, J.; Zhu, C.; Long, R.; Hao, W.; Chi, Z.; et al. Isolated single atom cobalt in Bi₃O₄Br atomic layers to trigger efficient CO₂ photoreduction. *Nat. Commun.* **2019**, *10*, 2840. [\[CrossRef\]](#)

Disclaimer/Publisher’s Note: The statements, opinions and data contained in all publications are solely those of the individual author(s) and contributor(s) and not of MDPI and/or the editor(s). MDPI and/or the editor(s) disclaim responsibility for any injury to people or property resulting from any ideas, methods, instructions or products referred to in the content.