Review

A Mini Review on Bismuth-Based Z-Scheme Photocatalysts

Ruizhen Li 1,2, Hanyang Chen 1, Jianrong Xiong 1, Xiaoying Xu 1, Jiajia Cheng 1, Xingyong Liu 3 and Guo Liu 2,4,*

1 School of Chemistry and Environmental Engineering, Sichuan University of Science and Engineering, Huixing Rd, Ziliujing District, Zigong 64300, China; liruizhen007@suse.edu.cn (R.L.); 17181020238@stu.suse.edu.cn (J.X.);
17181020239@stu.suse.edu.cn (X.X.); 18181030128@stu.suse.edu.cn (J.C.)
2 State Environmental Protection Key Laboratory of Synergetic Control and Joint Remediation for Soil & Water Pollution, Chengdu University of Technology, No. 1 Dongsan Road, Er’xian Bridge, Chengdu 610059, China
3 School of Chemical Engineering, Sichuan University of Science and Engineering, Huixing Rd, Ziliujing District, Zigong 64300, China; liuxy@suse.edu.cn
4 State Key Laboratory of Geohazard Prevention and Geoenvironment Protection, Chengdu University of Technology, No. 1 Dongsan Road, Er’xian Bridge, Chengdu 610059, China
* Correspondence: liuguo@cdut.edu.cn; Tel.: +86-133-0800-0115

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Abstract: Recently, the bismuth-based (Bi-based) Z-scheme photocatalysts have been paid great attention due to their good solar energy utilization capacity, the high separation rate of their photogenerated hole-electron pairs, and strong redox ability. They are considerably more promising materials than single semiconductors for alleviating the energy crisis and environmental deterioration by efficiently utilizing sunlight to motivate various photocatalytic reactions for energy production and pollutant removal. In this review, the traits and recent research progress of Bi-based semiconductors and recent achievements in the synthesis methods of Bi-based direct Z-scheme heterojunction photocatalysts are explored. The recent photocatalytic applications development of Bi-based Z-scheme heterojunction photocatalysts in environmental pollutants removal and detection, water splitting, CO2 reduction, and air (NOx) purification are also described concisely. The challenges and future perspective in the studies of Bi-based Z-scheme heterojunction photocatalysts are discussed and summarized in the conclusion of this mini review.

Keywords: Z-scheme photocatalysts; bismuth-based semiconductors; environmental remediation; energy production; photocatalytic applications

1. Introduction

The rapid growth of industry and the population has resulted in the over-consumption, unreasonable exploitation and utilization of fossil fuel resources. The global energy crisis and environmental deterioration have become two primary challenges of the 21st century in human society [1,2]. Therefore, it is necessary to develop renewable energy sources that can replace fossil fuels. As a powerful and inexhaustible renewable energy source, solar energy is considered as one of the best methods to mitigate these problems. It can be exploited and utilized for energy production (for example H2 [3–6], hydrocarbon fuel [7,8] and electric energy [9,10] production) and removal of pollutants (such as CO2 [11–15], organic contaminants in water [16–21] or air [22–26], emerging micropollutants [27,28]) by using photocatalytic, photovoltaic and other light-conversion technologies [29,30]. As one of the most promising light conversion technologies, photocatalytic technology only needs the appropriate
semiconductor photocatalyst and solar energy as energy input. In a typical photocatalytic procedure, the semiconductor photocatalysts can firstly absorb photons and be excited to generate hole-electron pairs under light irradiation. After separating and migrating to the surface of the photocatalysts, the two kinds of photo-generated charge carriers participate in redox reactions to produce free radicals and realize energy production or pollutant removal. However, the hole and electron can inevitably recombine in the bulk or on the surface of the photocatalysts, which is a disadvantageous factor [31]. In summary, the capacity of light absorption, the rate of photogenerated charge separation, migration and recombination are all influences on the photocatalytic process. The dominant factors can determine the photocatalytic efficiency of a given photocatalyst.

Research on semiconductor photocatalysts has attracted considerable attention since water splitting and hydrogen production on titanium dioxide (TiO2) were first reported by Fujishima et al. [32]. TiO2 is one of the most extensive studied semiconductors because of its chemical stability, non-toxicity, low cost, and good corrosion resistance [33,34]. Nevertheless, due to its wide bandgap (3.2 eV), TiO2 can only absorb ultraviolet light energy which constitutes about 4–5% of solar energy. The poor solar energy utilization capacity leads to the low quantum efficiency and the practical application of TiO2 is greatly limited [35,36]. Considering that visible light energy accounts for about 45% of sunlight energy [37], subsequently, in order to broaden the light-harvesting range, remarkable efforts have been devoted to explore visible light-activated semiconductors including CdSe, CdS, SiC, WO3, Fe2O3, Co3O4, g–C3N4, CdO, Ag2O etc. as photocatalysts, which possess a narrow band gap that is less than or equal to 3.0 eV. Recently, bismuth-based (Bi-based) semiconductors with advantages of non-toxicity, low cost and good thermal stability and as new and important visible light-activated semiconductors have become a research hotspot [20,38–48]. Bi-based semiconductors usually refer to the Bi3+ containing semiconductors because of the higher stability of Bi3+ than Bi5+. Various Bi-based semiconductors have been proved as excellent photocatalytic materials such as BiOX (X = Cl, Br, I) [49–51], BiVO4 [52], Bi2O3 [53], Bi2S3 [54], BiFeO3 [21], Bi2Sm2O7 [55], Bi2MoO6 [56], Bi2WO6 [24], CuBi2O4 [20], Bi3ClO4 [16], Bi2O2CO3 [23]. The bandgap structure of part of representative Bi-based semiconductors is summarized in Figure 1 [20,38–48]. As shown in Figure 1, the bandgap of the vast majority of Bi-based semiconductors is less than 3.0 eV except for BiPO4, BiOCl, Bi2O2CO3 and the like, which means that most Bi-based semiconductors can be excited by visible light. However, because of the valence band (VB) potential and the conduction band (CB) potential of Bi-based semiconductors with a narrow band gap not being positive and negative enough, the photogenerated holes and electrons do not have sufficient redox ability to drive the specific photocatalytic reactions, for example to produce free radicals including hydroxyl radical (OH) and superoxide radical (O2–), which is crucial for photocatalytic pollutant removal. Moreover, compared with wide-bandgap semiconductors, the excited electrons recombine with holes more easily and quickly in narrow-bandgap semiconductors. Among the Bi-based semiconductors shown in Figure 1, only BiPO4 has sufficient redox capacity to produce both OH and O2–, whereas BiPO4 has a larger bandgap, which is unfavorable for visible-light energy utilization. Consequently, two inherent limitations exist. One is that a given Bi-based semiconductor with a single component cannot have the strong redox ability and the good solar energy utilization capacity simultaneously. The other is that the recombination of the photogenerated electron-hole pairs inhibits the photocatalytic performance of a given Bi-based semiconductor with single component.

In recent years, tremendous attempts have been made to improve the visible-light absorption ability, light-harvesting efficiency, and photogenerated carriers’ separation of Bi-based semiconductors. Rongan He, Jiajiao Yu, and Wingkei Ho et al. have reviewed the strategies for enhancing the performance of bulk Bi-based semiconductors including component adjustment, morphology control, heterojunction construction, and surface modification [57]. Although the component adjustment, morphology control, and surface modification can improve the photocatalytic performance of bulk Bi-based semiconductors with a single component to some extent, the first inherent limitation is still not overcome. However, heterojunction construction, especially Z-scheme heterojunction construction, is considered a promising strategy to conquer the conflict between good solar energy utilization ability
and excellent redox capacity for single-component Bi-based semiconductor. From the development history of the Z-scheme heterojunction, it can be divided into three generations: liquid-phase Z-scheme, all-solid-state Z-scheme and direct Z-scheme photocatalyst [58]. Among them, the third generation Z-scheme heterojunction, direct Z-scheme photocatalyst, possesses the largest application range, the fastest charge-carrier migration rate, and the lowest fabrication cost because, unlike the first two generations with the help of electron mediator to transfer charge carriers, its charge-carrier migration driving force is the internal electric field which is formed due to the charge redistribution upon the contact of semiconductor components. The comprehensive description of the basic principle of the Z-scheme heterojunction can be found in some published review articles [59,60].

![Figure 1. The bandgap structure of part of representative Bi-based semiconductors.](image)

The present mini review focuses on recent achievements in a number of synthesis methods of Bi-based direct Z-scheme heterojunction photocatalysts and different photocatalytic applications of Bi-based Z-scheme heterojunction photocatalysts, such as photocatalytic degradation and electrocatalytic detection of environmental pollutants, water splitting, CO$_2$ reduction, and air (NOx) purification. Finally, the challenges, prospects, and future directions for Bi-based Z-scheme heterojunction photocatalysts are presented.

2. Synthesis Methods of Bi-Based Direct Z-Scheme Photocatalysts

Different synthesis methods can obtain Bi-based direct Z-scheme photocatalysts with different interfacial properties, geometrical configurations (see Figure 2), morphology, and crystallinity and so on, which eventually affect the photocatalytic performance of the prepared Bi-based direct Z-scheme photocatalysts. It is widely known that both morphology (size, shape and dimensionality) and crystallinity have a substantial influence on the properties of semiconductor oxides and further on the photocatalytic performance of the direct Z-scheme photocatalysts that they make up. In order to optimize the performance of semiconductor components, a variety of synthesis methods have been developed to control the morphology and crystallinity of semiconductor components by adjusting the parameters of synthesis methods. For example, Yongfa Zhu et al. [61] prepared a series of Bi$_2$MoO$_6$ with different morphologies (from 2D nanosheet to 1D microrod structures) by adjusting the pH value of the reactant through a hydrothermal method. Similarly, uniform BiOCl hierarchical microspheres assembled by nanosheets with tunable thickness were synthesized via a simple solvothermal route [62]. Bi$_2$O$_3$ with different hierarchitectures were reported to be controllably synthesized by modulating the experimental conditions of the template-free method, such as VO$_3^-$ concentration, the reaction temperature, and the pH values [63].
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Figure 2. The schematic diagram of (a) surface decorated structure; (b) Janus structure; and (c) core-shell structure.

However, for a direct Z-scheme photocatalyst, just optimizing the properties of its semiconductor components is not enough, the interfacial condition among the semiconductor components is crucial, considering the charge-carrier migration driving force of direct Z-scheme photocatalyst is related to the contact of semiconductor components. It is noteworthy that the stronger the interaction and intimate interface among the components of the Z-scheme heterojunction, the higher the efficiency of charge carrier separation and transfer [64]. Moreover, the geometrical configuration of direct Z-scheme photocatalyst is also important because it affects the contact mode of semiconductor components in Bi-based direct Z-scheme photocatalysts. In the surface decorated structure (Figure 2a), the components of the Bi-based Z-scheme heterojunction are all exposed to the reaction environment and can be excited by light and participate the redox reactions. However, excess amount of decorated component will inhibit the light absorption of other components, which can be improved by Janus structure (Figure 2b). In a core-shell structure (Figure 2c), the core component can be protected from light corrosion or undesired dissolution. Nevertheless, because of the protection, the core component cannot be excited by light and participate the redox reactions, which is not of benefit to the charge consumption and further charge carrier transfer between the core and shell component. Table 1 lists the advantages and shortcomings of extensively used synthesis methods of Bi-based direct Z-scheme photocatalysts including hydrothermal and solvothermal method, solid-state synthesis, deposition-precipitation method, cation exchange method, electrospinning method, self-assembly method, mechanical agitation method, and ultrasonic chemical method. The interfacial properties and geometrical configurations of the prepared Z-scheme heterojunction by these synthesis methods are also compared in Table 1 [65–69].
Table 1. Comparison of extensively used synthesis methods of direct Z-scheme photocatalysts.

| Synthesis Method                  | Advantages                                                                 | Shortcomings                                                                 | Interfacial Properties of the Prepared Z-Scheme Heterojunction | Geometrical Configurations of the Prepared Z-Scheme Heterojunction |
|-----------------------------------|-----------------------------------------------------------------------------|------------------------------------------------------------------------------|------------------------------------------------------------------|-------------------------------------------------------------------|
| Hydrothermal and Solvothermal Method | Controllable Size, High Crystallinity, Low Cost, Simple Operation, One-Pot Synthesis without Need of Post Annealing | High Requirements in Temperature, Pressure and Corrosion Resistance for Equipment, Required High Temperature | Strong Interaction and Intimate Interface                        | Surface-Decorated Structure                                       |
| Solid-State Synthesis             | High Synthetic Efficiency, Simple and Solvent-Free Synthetic Process         | High Energy Consumption, High Cost, Required High Temperature                | Strong Interaction and Intimate Interface                        | Surface-Decorated Structure                                       |
| Deposition-Precipitation Method   | Narrow Size Distributions of Products, Good Thermal Stability of Products    | Poor Reproducibility, Uncontrollable Deposition Location and Nucleation Site | Strong Interaction and Intimate Interface                        | Surface-Decorated Structure                                       |
| Cation Exchange Method            | Relatively Rapid Reaction Rate, Well-Preserved Initial Morphology, Size and Compositional Interfaces, High-Quality Nanocrystal, Simple and Flexible Method | Required Post Calcination Treatment                                           | Strong Interaction, High-Quality and Atomic-Precision Contact Interface | Janus, Surface-Decorated or more Complex Custom Structure Including Multicomponent Z-Scheme Heterojunction Structure |
| Electro-Spinning Method           | Facile and Simple Method, Simple Setup, Large Surface Area of Products       | Low Synthetic Efficiency, High Cost, Required Post-Heating Treatment          | Strong Interaction and Intimate Interface                        | Surface-Decorated Structure                                       |
| Self-Assembly Method              | Controllable Morphology and Size, Highly Ordered and Dispersive Products    | Low Yield, Poor Stability of Products                                         | Moderate Interaction                                            | Core-Shell, Surface-Decorated Structure                            |
| Mechanical Agitation Method       | Simple Setup, Straightforward Method, Avoiding the Use of Complex and Tedious Chemical and Thermal Treatments | Wide Size Distributions of Products, Poor Reproducibility, Uncontrollable Size | No Intimate Interface, Having Easily Detachable Components of Heterojunction, Low Crystallinity | Surface-Decorated Structure                                       |
| Ultrasonic Chemical Method        | Products, Rapid Reaction Rate, Controllable Morphology and Size             | High Cost, Hard to Scaling Up                                                | Strong Interaction and Intimate Interface                        | Surface-Decorated or Core-Shell Structure                           |
In the tables of Section 3, we summarize the representative examples of the aforementioned synthesis methods of Bi-based direct Z-scheme photocatalysts from recent related works.

3. Applications of Bi-Based Z-Scheme Photocatalysts

Due to the excellent redox capacity, good solar energy utilization ability, and efficient hole-electron separation ability, superior photocatalytic performance, Bi-based Z-scheme heterojunctions have been achieved in a wide range of applications, such as degradation of pollutants [70], water splitting [68], CO₂ reduction [71], detection of environmental pollutants [72], removal of NOₓ [73], etc. In this section, various photocatalytic applications of Bi-based Z-scheme photocatalysts are summarized and briefly presented.

3.1. Degradation of Pollutants in Water

With the rapid development of the economy, large-scale industrialization and urbanization make environmental pollution a very serious problem, which not only hinders the sustainable development of society, but also threatens the life and safety of human beings [74]. Owing to the unique structure of a Bi-based Z-scheme photocatalyst, the redox potential of the heterojunction can be maximized, the solar energy can be almost utilized completely, and the photogenerated electrons and holes can be separated efficiently. The Bi-based Z-scheme photocatalyst is reported to be a promising photocatalyst for photocatalytic degradation of various environmental pollutants. Table 2 lists some of the latest and most representative research on degradation of pollutants by Bi-based Z-scheme photocatalyst. As shown in Table 2, the photocatalytic efficiency usually was expressed by the degradation rate of pollutants (%) or the kinetic constant k (min⁻¹). It has been shown that compared with corresponding single Bi-based photocatalyst, the Z-scheme heterojunction greatly improves the photocatalytic degradation efficiency of pollutants. For example, Liu et al. [75] prepared Z-scheme Bi₃O₄Cl/CdS by the simple hydrothermal method. Briefly, CdS nanospheres and Bi₃O₄Cl nanosheets were synthesized firstly by the hydrothermal method. Then, with the assist of polyvinyl pyrrolidone (PVP), Z-scheme Bi₃O₄Cl/CdS was synthesized by a facile surfactant-free hydrothermal treatment. The results showed that the CdS nanospheres are successfully and uniformly loaded on the surface of Bi₃O₄Cl nanosheets forming a surface-decorated heterostructure and an efficiently intimate heterojunction interface (see Figure 3a). The heterojunction presents an obviously enhanced absorption in the visible region compared to pure Bi₃O₄Cl. The significant improvement of charge transfer and separation of the composite was proved by photocurrent (see Figure 3b) and electrochemical impedance spectra (EIS) measurements. Under visible light illumination, Bi₃O₄Cl/CdS composite displays higher photocatalytic activity towards the ciprofloxacin (CIP) and tetracycline (TC) degradation than pure Bi₃O₄Cl, which is ascribed to the direct Z-scheme mechanism (See Figure 3c). The direct Z-scheme mechanism was proved by active species trapping experiments and electron spin resonance (ESR) technology. As shown in Figure 3c, the redox potential of the Z-scheme Bi₃O₄Cl/CdS heterojunction can be maximized sufficiently to produce OH (2.40 V vs. NHE (normal hydrogen electrode)) and O₂⁻ (−0.33 V vs. NHE).
Table 2. Research progress on Bi-based Z-Scheme photocatalysts applied in photocatalytic degradation.

| Photo-Catalyst         | Synthesis Method          | Light Source                      | Catalyst Dose | Pollutants                      | Photocatalytic Efficiency | Ref.       |
|------------------------|---------------------------|-----------------------------------|----------------|---------------------------------|---------------------------|-----------|
| Bi$_2$WO$_6$/CuBi$_2$O$_4$ | Hydro-Thermal             | 300 W Xe Lamp ($\lambda \geq$ 400 nm) | 0.5 mg/mL     | Tetracycline (15 mg/L, 100 mL)  | 0.0393 min$^{-1}$ (CuBi$_2$O$_4$ 0.0054 min$^{-1}$) | [70]      |
| BiOI/g–C$_3$N$_4$      | In situ Reduction and Oxidation | 60 W LED (Light Emitting Diode) Lamp ($\lambda >$ 400 nm) | 3.33 mg/mL    | Phenol (100 mg/L, 15 mL)       | 60% (BiOI 20%)            | [76]      |
| CdS/BiOI               | Hydro-Thermal             | 300 W Xe Lamp ($\lambda >$ 420 nm) | 0.2 mg/mL     | RbB (20 mg/L, 100 mL)          | 0.03945 min$^{-1}$ (BiOI 0.00398 min$^{-1}$) | [77]      |
| BiOBr/Bi$_2$MoO$_6$    | Co-Precipitation          | 300 W Xe Lamp ($\lambda \geq$ 420 nm) | 0.2 mg/mL     | Ciprofloxacin (10 mg/L, 50 mL), RbB (10 mg/L, 50 mL) | 84.63% (Bi$_2$MoO$_6$ 15.21%); 0.37613 min$^{-1}$ (Bi$_2$MoO$_6$ 0.00689 min$^{-1}$) | [78]      |
| Bi$_2$O$_3$/g–C$_3$N$_4$ | Solid-State Synthesis     | 500 W Xe Lamp ($\lambda >$ 400 nm) | 1.0 mg/mL     | MB (1.1 $\times$ 10$^{-5}$ mol/L, 300 mL); RbB (1.0 $\times$ 10$^{-5}$ mol/L, 300 mL) | 0.0253 min$^{-1}$ (g–C$_3$N$_4$ 0.0074 min$^{-1}$); 0.0101 min$^{-1}$ (g–C$_3$N$_4$ 0.0002 min$^{-1}$) | [79]      |
| Bi$_2$Fe$_4$O$_9$/Bi$_2$WO$_6$ | Hydro-Thermal            | 300 W Xe lamp ($\lambda \geq$ 420 nm), 350 W Xe lamp (cut off UV and IR light) | 0.3 mg/mL     | RbB (10 mg/L, 100 mL)          | 0.0380 min$^{-1}$ (Bi$_2$Fe$_4$O$_9$ 0.0015 min$^{-1}$) | [74]      |
| AgI/Bi$_2$O$_7$I       | Ion Exchange              | 1.0 mg/mL (cut off UV and IR light) | 1.0 mg/mL     | RbB (10 mg/L, 100 mL)          | 0.046 min$^{-1}$ (Bi$_2$O$_7$I 0.012 min$^{-1}$) | [80]      |
| AgI/Bi$_2$WO$_6$        | Precipitation             | 300 W Xe lamp ($\lambda \geq$ 420 nm) | 0.3 mg/mL     | Tetracycline (20 mg/L, 100 mL)  | 0.075 min$^{-1}$ (Bi$_2$WO$_6$ 0.014 min$^{-1}$) | [81]      |
| AgBr/CuBi$_2$O$_4$      | Precipitation             | 300 W Xe lamp ($\lambda \geq$ 420 nm) | 0.5 mg/mL     | Tetracycline (10 mg/L, 100 mL)  | 0.03551 min$^{-1}$ (CuBi$_2$O$_4$ 0.00238 min$^{-1}$) | [82]      |
| TCPP/rGO/Bi$_2$WO$_6$   | Ultrasonic Chemical       | 300 W Xe lamp ($\lambda >$ 420 nm) | 0.3 mg/mL     | Tetracycline (15 mg/L, 100 mL)  | 83.60% (Bi$_2$WO$_6$ 48.61%) | [83]      |
### Table 2. Cont.

| Photo-Catalyst                  | Synthesis Method           | Light Source                        | Catalyst Dose | Pollutants                              | Photocatalytic Efficiency          | Ref. |
|--------------------------------|----------------------------|-------------------------------------|---------------|-----------------------------------------|------------------------------------|------|
| Ag$_3$PO$_4$/CuBi$_2$O$_4$      | Precipitation              | 300 W Xe lamp ($\lambda > 420$ nm) | 0.5 mg/mL     | Tetracycline (10 mg/L, 100 mL)          | 0.0201 min$^{-1}$ (CuBi$_2$O$_4$  | [84] |
|                                |                            |                                     |               |                                         | 0.0072 min$^{-1}$)                 |      |
| Porous g–C$_3$N$_4$/BiOI       | Hydro-Thermal              | 50 W 410 nm LED light arrays        | 1 mg/mL       | MB (20 mg/L, 30 mL)                     | 0.0160 min$^{-1}$ (BiO)            | [85] |
|                                |                            |                                     |               |                                         | 0.0041 min$^{-1}$)                 |      |
| CdS/Bi$_2$O$_4$Cl               | Hydro-Thermal              | 250 W Xe lamp ($\lambda > 420$ nm) | 0.5 mg/mL     | Tetracycline (10 mg/L, 100 mL). Cipro-Floxacin (10 mg/L, 100 mL) | 0.0643 min$^{-1}$ (Bi$_2$O$_4$Cl  | [75] |
|                                |                            |                                     |               |                                         | 0.0148 min$^{-1}$)                 |      |
|                                |                            |                                     |               |                                         | 0.0151 min$^{-1}$)                 |      |
| Cu$_2$O/Bi$_2$O$_7$I            | Glucose Reduction Reaction | 500 W Xe lamp                      | 1 mg/mL       | RhB (10 mg/L, 100 mL)                   | 0.0233 min$^{-1}$ (Bi$_2$O$_7$I  | [86] |
|                                |                            |                                     |               |                                         | 0.00736 min$^{-1}$)                |      |
| CuInS$_2$/Bi$_2$WO$_6$          | Hydro-Thermal              | 300 W Xe lamp ($\lambda \geq 420$ nm) | 0.3 mg/mL     | Tetracycline Hydrochloride (10 mg/L, 100 mL) | 0.0176 min$^{-1}$ (Bi$_2$WO$_6$  | [87] |
|                                |                            |                                     |               |                                         | 0.01473 min$^{-1}$)                |      |
| MoO$_3$/Bi$_2$O$_4$             | Hydro-Thermal              | 100 W LED lamp ($\lambda = 420$ nm) | 0.5 mg/mL     | RhB (10 mg/L, 100 mL)                   | 99.6% (Bi$_2$O$_4$ 73%)            | [88] |
|                                |                            |                                     |               |                                         | 0.090 min$^{-1}$ (BiO)            | [89] |
|                                |                            |                                     |               |                                         | 0.003 min$^{-1}$)                 |      |
| BiO/Bi$_2$O$_4$                 | Ultrasonic Chemical        | 100 W LED lamp                      | 0.5 mg/mL     | RhB (10 mg/L, 100 mL)                   | 95.3% (Bi$_2$O$_4$ 32.7%)          | [90] |
|                                |                            |                                     |               |                                         | (Bi$_2$O$_4$ 32.7%)                |      |
| Bi$_2$MoO$_6$/TiO$_2$           | Hydro-Thermal              | 800 W Xe lamp                       | 0.6 mg/mL     | 4-Nitrophenol (50 mg/L, 100 mL)         | 0.043 min$^{-1}$ (Bi$_2$MoO$_6$  | [91] |
|                                |                            |                                     |               |                                         | 32.7%)                             |      |
| Bi$_2$WO$_6$/Porous g–C$_3$N$_4$ | Ultrasonic Chemical       | 500 W Wolfram lamp ($\lambda \geq 420$ nm) | 0.5 mg/mL     | RhB (10 mg/L, 100 mL)                   | 0.013 min$^{-1}$ (Bi$_2$WO$_6$  | [91] |
|                                |                            |                                     |               |                                         | 0.013 min$^{-1}$)                 |      |
| Bi$_2$WO$_6$/BiOI               | Hydrothermal               | 500 W Xe lamp ($\lambda > 420$ nm) | 1 mg/mL       | RhB (10 mg/L, 40 mL)                    | 0.03 min$^{-1}$ (BiO)             | [92] |
|                                |                            |                                     |               |                                         | 0.002 min$^{-1}$)                 |      |
| Ag$_3$PO$_4$/Bi$_2$WO$_6$       | Precipitation              | 50 W LED lamp ($\lambda = 410$ nm)  | 1 mg/mL       | MB (20 mg/L, 30 mL)                     | 0.61 min$^{-1}$ (Bi$_2$WO$_6$ 10 min$^{-1}$) | [93] |
|                                |                            |                                     |               |                                         | 0.09672 min$^{-1}$ (BiVO$_4$ 0.01101 min$^{-1}$) |      |
| g–C$_3$N$_4$/BiVO$_4$           | Hydrothermal               | 250 W Xe lamp ($\lambda > 420$ nm)  | 0.2 mg/mL     | MO (20 mg/L, 50 mL)                     | 0.02 min$^{-1}$ (BiVO$_4$ 0.0016 min$^{-1}$) | [94] |
Zeng et al. [83] fabricated ternary Z-scheme heterojunction (meso-tetra (4–carboxyphenyl) porphyrin (TCPP)/reduced graphene oxide (rGO)/Bi2WO6 (BWO)) via an ultrasonic chemical method. Firstly, rGO/BWO was prepared by the hydrothermal method. Then, rGO/BWO was added to absolute ethanol and ultrasonicated for dispersal. TCPP was added to the above suspension and kept in ultra-sonication then stirred until the solvent was completely volatilized. Finally, the product was dried to obtain the TCPP/rGO/BWO. During the synthetic process, the carboxylic groups of TCPP make it combine with the BWO tightly. The introduction of rGO further improves the photocatalytic performance of the composite because of its \( \pi-\pi \) structure for efficient contaminants adsorption, great photo-response property for expanding visible-light response range, and high electron mobility for promoting charge transfer and separation. The structure of the prepared TCPP/rGO/BWO is a surface-decorated heterostructure, which was proved by scanning electron microscopy (SEM) results. The TCPP0.25/rGO/BWO has the best photocatalytic performance for the degradation of tetracycline (TC) compared with BWO, rGO/BWO, TCPP/BWO, and other TCPP/rGO/BWO composites with different TCPP contents. The results of trapping experiments and ESR analysis indicated that the h\(^{+}\) and O\(_2\)• are the major contributors for the TC decomposition in the TCPP0.25/rGO/BWO system. The O\(_2\)• can only be produced via reducing O\(_2\) by the electrons at the lowest unoccupied molecular orbital (LUMO) (–0.60 eV) of TCPP which is above the energy level of the O\(_2\)/O\(_2\)• (–0.33V vs. NHE). Therefore, a Z-scheme mechanism is proposed to elucidate the charge transfer process in the TCPP0.25/rGO/BWO system to ensure the efficient charge separation and sufficient redox potential.
3.2. Water Splitting

Solar-water splitting can convert solar energy into clean, carbon-neutral and storable chemical energy (hydrogen fuel) without using fossil fuels and causing carbon emissions. Therefore, solar-water splitting has attracted much attention [95].

The photocatalytic (PC) and photoelectrocatalytic (PEC) methods are two simple, efficient, low-cost and environmentally benign means for achieving solar-water splitting. As shown in Figure 4a, during the photocatalytic process, the photocatalysts that are highly dispersed in solution can be excited by solar light and produce electron-hole pairs which further participate in the redox reactions to split water to hydrogen (H\textsubscript{2}) and oxygen (O\textsubscript{2}). Unlike in the PC system where photocatalysts are dispersed in the solution, in the PEC system the photocatalysts should be attached on the working electrode to construct the PEC system and in order to apply an external bias. Although the external bias is beneficial to promote the charge separation and reaction kinetics and attached photocatalysts are easy to reuse, the specific surface area and the photocatalytic active sites of attached photocatalysts on the electrode is far less than dispersed photocatalysts in the solution. In the PEC water splitting system, at least one photoelectrode should be required for utilizing solar energy. Depending on the type of photocatalyst on the photoelectrode, PEC water splitting system has different hydrogen production principles. As displayed in Figure 4b, when the photoelectrode consisting of n-type semiconductor photocatalyst as photoanode as excited by solar energy, the photogenerated holes will oxidise water molecule to hydrogen ions and O\textsubscript{2}, see Equation (1). The photogenerated electrons will transfer to the counter electrode (cathode) via an external circuit to reduce the hydrogen ions to hydrogen, see Equation (2) [96]. By contrast, when the photocatalyst is p-type semiconductor and as photocathode, the H\textsubscript{2} and O\textsubscript{2} will evolve at the surface of photocathode (see Equation (2)) and anode (see Equation (1)), respectively (see Figure 4c). The two basic semi-reactions and their overall reaction (Equation (3)) are as follows:

\[
\begin{align*}
\text{anode:} & \quad 2\text{H}_2\text{O} + 4h^+ \rightarrow \text{O}_2 + 4\text{H}^+ \quad (E_{\text{OX}}^0 = +1.23 \text{ V at pH} = 7) \\
\text{cathode:} & \quad 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \quad (E_{\text{RED}}^0 = 0 \text{ V at pH} = 0) \\
\text{Overall:} & \quad 2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2
\end{align*}
\]

\[\text{Figure 4. Schematic diagram of photocatalytic hydrogen production principle of photocatalyst dispersed in electrolyte (a), schematic diagram of hydrogen production principle in a photoelectrocatalytic system composed of a n-type semiconductor as photoanode (b), and a p-type semiconductor as photocathode (c), respectively.}\]

According to the aforementioned semi-reactions, in order to realize overall water splitting, the selected ideal photocatalyst should satisfy the requirements that the CB edge potential of the photoelectrode semiconductor should be above the energy level of the H\textsuperscript{+}/H\textsubscript{2} (0 V vs. NHE at pH = 0) and the VB edge potential should be below the energy level of the O\textsubscript{2}/H\textsubscript{2}O (1.23 V vs. NHE at pH = 0) [97]. The Z-scheme heterojunction provides a promising way to overcome the thermodynamic energy barrier for solar-water splitting by combining a narrow bandgap semiconductor which ensures the maximized utilization solar energy and one or more paired semiconductors with appropriate energy...
band structure to broaden the redox range of the photocatalyst composite. Bi-based semiconductors are promising candidates for a Z-scheme heterojunction attributed to their unique energy band structure and other attractive advantages. Table 3 summarizes the latest development of Bi-based Z-scheme photocatalysts applied for solar-water splitting. The Bi-based Z-scheme photocatalyst and its synthesis method, the conditions of the solar-water splitting process, the utilization of co-catalyst, the products and yields, and apparent quantum yield (AQY) of all the examples are presented in Table 3. From the data of Table 3, it is seen that Bi-based Z-scheme photocatalysts exhibit promising performance for solar-water splitting. Most research using Bi-based Z-scheme photocatalysts can obtain good H₂ evolution yield. Chou et al. [98] made SnS₂ self-growth on the BiPO₄ nanosheets to form three dimensions (3D) flower heterogeneous composite by a multi-step solvothermal method. According to the radical-trapping experiment results and band structure analysis, a Z-scheme heterojunction was formed between SnS₂ and BiPO₄. Under visible light, the formed Z-scheme heterojunction showed the highest H₂ evolution rate of 303 µmol h⁻¹ g⁻¹, which is about 1.43 and 2.01 times higher than that of pure SnS₂ and pure BiPO₄, respectively.

Table 3. Research progress of Bi-based Z-Scheme photocatalyst applied in solar-water splitting.

| Photo-Catalyst | Co-Catalyst | Synthesis Method | Experimental Conditions | Products and Yields | AQY | Ref. |
|----------------|-------------|------------------|-------------------------|---------------------|-----|-----|
| BiPO₄/SnS₂      | No          | Hydrothermal     | Visible light irradiation (λ > 380 nm). Pure Water 300 W Xe Lamp | H₂: 303 µmol h⁻¹ g⁻¹ | –   | [98] |
| Bi/BiSeO₃/SnS₂O₄ | Bi          | Hydrothermal     | (λ > 400 nm). 20% CH₃OH Solution Xe lamp (AM (air mass) 1.5); 0.5 M Na₂HPO₄/NaH₂PO₄ Solution | H₂: 325.9 µmol h⁻¹ g⁻¹ | –   | [99] |
| Cu₃P/Bi₂WO₆     | No          | Mechanical Agitation | | H₂: 4.65 µmol h⁻¹ g⁻¹ O₂: 2.3 µmol h⁻¹ g⁻¹ | –   | [68] |
| BiVO₄/Black phosphorus | 5 wt% Co₃O₄ | Self-Assembly | 320 W Xeon Lamp (λ > 420 nm). Pure Water | H₂: 160 µmol h⁻¹ g⁻¹ O₂: 102 µmol h⁻¹ g⁻¹ | 0.89% at 420 nm | [100] |
| Bi₂O₃/Bi₂S₃     | 1 wt% Pt    | Wet Chemistry    | 500 W Xeon Lamp; 0.1 M Na₂S/Na₂SO₃ Solution | H₂: 62.61 µmol h⁻¹ | –   | [101] |
| g-C₃N₄/BiFeO₃   | No          | Solid-State Synthesis | Pressure Hg Lamps (UV). Pure Water 300 W Xe Lamp (λ > 420 nm); 20 vol.% Lactic Acid Solution | H₂: 160.75 µmol h⁻¹ g⁻¹ O₂: 80.12 µmol h⁻¹ g⁻¹ | –   | [102] |
| Cds/BiVO₄       | 2 wt% Pt    | Solvothermal     | 350 W Xe Lamp (λ > 420 nm); 30 vol.% Na₂S and 0.25 M Na₂SO₃ Solution | H₂: 1153 µmol h⁻¹ | –   | [103] |
| Bi₂S₃/MoS₂/TiO₂ | No          | Microwave-Assisted Hydrothermal | 250 W Xe Lamp (λ ≥ 420 nm) | H₂: 2195 µmol h⁻¹ g⁻¹ | –   | [104] |
| Cs₂O/Bi₂O₃/ZnO  | No          | Solution Combustion Method | Xe Lamp (AM 1.5 G); Pure Water | H₂: 149.5 µmol h⁻¹ g⁻¹ O₂: 73.2 µmol h⁻¹ g⁻¹ | 1.68% at 365 nm 0.92% at 420 nm | [105] |
| ZnIn₂S₄/RGO/BiVO₄ | 1 wt% Pt  | Hydrothermal     | 350 W Xe Lamp (λ > 420 nm); 5 mol L⁻¹ HCHO Solution Xe Lamp (λ > 420 nm); Pure Water | H₂: 1687 µmol h⁻¹ g⁻¹ | 22.91% | [106] |
| RGO–Cu₃O/Bi₂WO₆ | No          | Solvothermal     | 300 W Xeon Arc Lamp (λ > 420 nm); TC Solution | H₂: 1.80 µmol h⁻¹ g⁻¹ | –   | [107] |
| Cu₃O/RGO/BiVO₄  | –           | Solvothermal     | | H₂: 5.90 µmol h⁻¹ g⁻¹ | –   | [108] |
Due to the high energy barrier of its four-electron transfer process, the O₂-evolution half reaction in overall solar-water splitting is much more challenging than the H₂-evolution half reaction, which dramatically suppresses the efficiency of the overall solar-water splitting. Usually, most semiconductor photocatalysts have low activity for O₂ evolution [109]. Besides the overall solar-water splitting, H₂-evolution half reaction using a sacrificial agent is another efficient way to harvest and convert solar energy to H₂. The sacrificial agent plays a significant role in the H₂-evolution half reaction. Suitable sacrificial reagents can improve the H₂-evolution efficiency remarkably by scavenging the photogenerated holes to reduce the charge carrier recombination significantly. Zhu et al. investigated the effect of the different organic compounds on the hydrogen production rate of ZnIn₂S₄/RGO/BiVO₄ [106]. As shown in Figure 5a, in the presence of organic compounds such as formaldehyde, methanol, formic acid, acetaldehyde and ethanol and so on, the hydrogen production rate has been promoted to a different extent. Organic compounds including alcohols (for example methanol [99]), aldehydes (for example formaldehyde [106]), organic acids (for example lactic acid [103]) have been extensively used as efficient hole scavengers for H₂ production in Bi-based Z-scheme photocatalysts systems.

![Figure 5. (a) Effects of different organic compounds on hydrogen production in ZnIn₂S₄/RGO/BiVO₄ photocatalyst. Reproduced with permission from [106]. Copyright Elsevier, 2019. (b) Photocatalytic H₂ generation rates of different mass ratios CdS/BiVO₄ in lactic acid solution with or without 2 wt.% Pt under visible light irradiation. Reproduced with permission from [103]. Copyright Elsevier, 2017.](image)

Furthermore, owing to the sufficient redox ability of the Bi-based Z-scheme photocatalyst, even refractory organic pollutants can also be successfully used as hole scavengers to achieve simultaneous H₂ generation and pollutant degradation. Very recently, Liu et al. constructed a Cu₃O/BiVO₄ Z-scheme heterojunction by using reduced graphene oxide (rGO) as an adhesive via a two-step solvothermal method. This Bi-based Z-scheme photocatalyst exhibits excellent photocatalytic performance on simultaneous tetracycline (TC) degradation and H₂ production under visible light irradiation [108].
Moreover, the introduction of a suitable co-catalyst can further improve the solar-water splitting efficiency of a Bi-based Z-scheme photocatalyst. The reason for this improvement may be attributed to the fact that co-catalysts can efficiently collect photogenerated carriers and catalyze H₂ or O₂ evolution as well as improve the stability of photocatalysts by suppressing photocorrosion [111]. Usually, noble metals and especially Pt have been extensively used as co-catalyst for solar-water splitting [111]. For example, Zhou et al. [103] prepared hierarchical CdS/BiVO₄ hybrid composed of CdS nanoparticles decorated on BiVO₄ nanowires (NWs) by the solvothermal method. The strongly chemical interaction between CdS and BiVO₄ was confirmed by XPS (X-ray photoelectron spectroscopy) results. As illustrated in Figure 5b, under visible light irradiation and in a lactic acid electrolyte, no hydrogen generation was observed on pure BiVO₄ even loaded with Pt as co-catalyst, attributed to the CB edge potential of pure BiVO₄ being lower than the energy level of H⁺/H₂. The bare CdS showed a weak hydrogen production capacity. After forming a CdS/BiVO₄ Z-scheme heterojunction, the hydrogen production capacity was enhanced, whereas the improvement of photocatalytic H₂ activity was by orders of magnitude after loading Pt. At an optimized condition, CdS (50 wt.%) /BiVO₄ NWs with loading 2 wt.% Pt exhibited the fastest photocatalytic H₂ generation rate which is 9.30 times of that of CdS (50 wt.%)/BiVO₄ NWs without loading Pt co-catalyst. Therefore, due to their low overpotential for H₂ evolution and excellent electron-accepting capacity, using noble metal as a co-catalyst is an effective method to improve the photocatalytic hydrogen evolution, which is conducive to the electron generated by the photocatalyst to transfer to the noble metal to catalyze H₂ evolution.

However, the high price and scarcity of noble metals limit their large-scale practical application in photocatalytic H₂ generation as co-catalysts. In recent years, many efforts were devoted to develop co-catalysts composed of abundant and inexpensive elements to assist Bi-based Z-scheme photocatalyst for solar-water splitting. Recently, Xu et al. [99] prepared Bi/Bi₂O₃/Sn₃O₄ by hydrothermal method (See Figure 6a). The band structure of Bi₃O₇I matches well with that of Sn₃O₄ to constitute a direct Z-scheme heterojunction. Metallic Bi which is evenly covered on the surface of Z-scheme Bi₃O₇I/Sn₃O₄ photocatalyst and comes from the reduction reaction between Sn₃O₄ and Bi₂O₇I during the synthesis process was demonstrated to be a good substitute for noble metals as co-catalyst to further improve the H₂ generation and extend the light absorption range. The X-ray diffraction (XRD) results (see Figure 6b) confirmed the presence of Bi metal. As shown in Figure 6b, as increasing the amount of Bi₂O₇I, the characteristic peak of Bi gradually appears and increases. The photocatalytic hydrogen production experiments under visible light irradiation demonstrated that the highest hydrogen evolution of this Z-scheme catalyst reached 325.9 μmol h⁻¹·g⁻¹ without any noble metal co-catalyst and exceeded the rate on pure Sn₃O₄ by 5 times (See Figure 6c).

Great processes have been made to construct double Z-scheme heterojunction structures to make full use of solar energy to apply in water splitting. Drmosh et al. [104] prepared Bi₂S₃/MoS₂/TiO₂ (MBT) by a facile microwave-assisted hydrothermal method. The double Z-scheme heterojunction structure was constructed due to the matched band structure among Bi₂S₃ nanorods, MoS₂ nanometer sheets and TiO₂ nanotubes. As exhibited in Figure 6d, photogenerated electrons in the CB of TiO₂ can recombine with photogenerated holes in the VB of MoS₂, and photogenerated electrons in the CB of MoS₂ can recombine with photogenerated holes in the VB of Bi₂S₃, preserving the photogenerated electrons and holes with the strongest reduction and oxidation power. The constructed direct double Z-scheme heterojunction extends the light-harvesting capability, couples the respective advantages of each component, and efficiently separates photogenerated electron-hole pairs. The optimized Bi₂S₃/MoS₂/TiO₂ nanocomposites presented a high photocatalytic H₂-production rate of 2195 μmol h⁻¹·g⁻¹ under the sunlight irradiation, even in the absence of any noble-metal cocatalyst (See Figure 6e).
Great processes have been made to construct double Z-scheme heterojunction structures to make full use of solar energy to apply in water splitting. Drmosh et al. [104] prepared Bi$_2$S$_3$/MoS$_2$/TiO$_2$ (MBT) by a facile microwave-assisted hydrothermal method. The double Z-scheme heterojunction structure was constructed due to the matched band structure among Bi$_2$S$_3$ nanorods, MoS$_2$ nanometer sheets and TiO$_2$ nanotubes. As exhibited in Figure 6d, photogenerated electrons in the CB of TiO$_2$ can recombine with photogenerated holes in the VB of MoS$_2$, and photogenerated electrons in the CB of MoS$_2$ can recombine with photogenerated holes in the VB of Bi$_2$S$_3$, preserving the photogenerated electrons and holes with the strongest reduction and oxidization power. The constructed direct double Z-scheme heterojunction extends the light-harvesting capability, couples the respective...
3.3. CO$_2$ Reduction

Nowadays, excessive carbon dioxide (CO$_2$) emission is a key reason for global warming. Proposing environmentally friendly and efficient strategies to dramatically reduce atmospheric CO$_2$ is essential and urgent. Photocatalysis seems a propitious and appealing strategy because it can directly make use of inexhaustible solar energy to convert CO$_2$ in the atmosphere into hydrocarbons such as CH$_4$, HCOOH, CO, CH$_2$O and CH$_3$O (Equations (4)–(9)) [33,112], alleviating the greenhouse effect and energy crisis simultaneously. The product species of photocatalytic CO$_2$ reduction depend on the relationship between the CB edge potential of the photocatalyst and the reduction potentials of the desired CO$_2$ reduced product. Since CO$_2$ is well known as one of the most thermodynamically stable chemical species [113,114], to satisfy thermodynamic requirements, the more negative the CB edge potential of the photocatalyst, the higher the possibility to drive the CO$_2$ reduction process. On the other hand, the photocatalytic CO$_2$ reduction system ultimately needs the use of water as the electron source (Equation (10)); a semiconductor photocatalyst has to satisfy band edge potentials that straddle both the water oxidation and CO$_2$ reduction potentials.

\[
\begin{align*}
\text{CO}_2 + 8\text{H}^+ + 8\text{e}^- & \rightarrow \text{CH}_4 + 2\text{H}_2\text{O} \quad E^0 = -0.24 \text{ V vs NHE at pH} = 7 \quad (4) \\
\text{CO}_2 + 6\text{H}^+ + 6\text{e}^- & \rightarrow \text{CH}_3\text{OH} + \text{H}_2\text{O} \quad E^0 = -0.38 \text{ V vs NHE at pH} = 7 \quad (5) \\
\text{CO}_2 + 4\text{H}^+ + 4\text{e}^- & \rightarrow \text{HCHO} + \text{H}_2\text{O} \quad E^0 = -0.48 \text{ V vs NHE at pH} = 7 \quad (6) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{CO} + \text{H}_2\text{O} \quad E^0 = -0.53 \text{ V vs NHE at pH} = 7 \quad (7) \\
\text{CO}_2 + 2\text{H}^+ + 2\text{e}^- & \rightarrow \text{HCOOH} \quad E^0 = -0.61 \text{ V vs NHE at pH} = 7 \quad (8) \\
\text{CO}_2 + \text{e}^- & \rightarrow \cdot\text{CO}_2^- \quad E^0 = -1.90 \text{ V vs NHE at pH} = 7 \quad (9) \\
\text{H}_2\text{O} + 2\text{h}^+ & \rightarrow 2\text{H}^+ + 1/2\text{O}_2 \quad E^0 = +0.82 \text{ V vs NHE at pH} = 7 \quad (10)
\end{align*}
\]

The photocatalytic CO$_2$ reduction reaction usually includes four main steps as follows: (1) CO$_2$ adsorption process on the active sites of photocatalyst; (2) absorption of sufficient incident photon energy by the photocatalyst to generate electron-hole pairs; (3) charge separation and migration to the surface of the photocatalyst; (4) surface reactions for CO$_2$ reduction and products desorption. In order to efficiently photocatalytically reduce CO$_2$, the photocatalyst should possess all the features to successfully achieve each above step: including strong CO$_2$ selective adsorption capacity, broad light response range, high charge separation efficiency, and sufficiently strong redox activity. Due to the aforementioned last three virtues, Z-scheme photocatalytic systems have been extensively investigated and applied for CO$_2$ reduction in recent years. Based on the prominent photocatalytic activity nature of bismuth semiconductor, the representative progresses of Bi-based Z-scheme photocatalytic systems for the application of CO$_2$ reduction are summarized in Table 4.
Table 4. The research progress of Bi-based Z-scheme photocatalyst in CO₂ reduction.

| Photo-Catalyst | Co-Catalyst | Synthesis Method | Conditions | Products and Yields | Ref. |
|----------------|-------------|------------------|------------|---------------------|------|
| CdS/BiVO₄      | No          | Deposition       | 300 W Xenon Arc Lamp (λ > 400 nm). 20 mg Photocatalyst in 180 mL Stainless Steel Reactor with Quartz Window; Filled with CO₂ (0.3 Pa). | CH₄: 1.75 µmol h⁻¹ g⁻¹ CO: 0.39 µmol h⁻¹ g⁻¹ | [115] |
| BiOI/g-C₃N₄    | No          | Deposition       | 300 W Xenon Arc Lamp (λ > 400 nm); 0.1 g Photocatalyst in 180 mL Stainless Steel Cylindrical Vessel with Quartz Window; Introducing CO₂ and H₂O Vapor by Bubbling Approach. | CH₄: 1.76 µmol h⁻¹ g⁻¹ CO: 22.21 µmol h⁻¹ g⁻¹ NO: 20.66 µmol h⁻¹ g⁻¹ | [116] |
| Bi₂WO₆/TiO₂    | No          | Electrostatic Self-Assembly | 300 W Xenon Arc Lamp (780 nm > λ > 320 nm); 20 mg Photocatalyst in 25 mL Quartz Reactor; CO₂ was Evacuated by a Mechanical Pump. | CH₄: 10.8 µmol h⁻¹ g⁻¹ CO: 25.8 µmol h⁻¹ g⁻¹ | [117] |
| g-C₃N₄∥Bi₂O₂[BO₃(OH)] | No | Solid-State Synthesis | 20 mg Photocatalyst; 1.7 g Na₂CO₃ Treated with 15 mL H₃SO₄ (0.1 mol/L) to in situ Generate CO₂. 300 W Xenon Arc Lamp (λ > 420 nm); 100 mg Catalyst in 500 mL Reactor; Introducing CO₂ and H₂O Vapor by Bubbling Approach. 180 mW/cm² Solar Light (λ < 800 nm); 300 W Xe Lamp; 0.02 g Photocatalyst and 2 mL H₂O in Reactor; Filled with CO₂. The Reactor was Heated to 393 K. | CO: 6.09 µmol h⁻¹ | [118] |
| Bi₂WO₆∥g-C₃N₄  | No          | Hydrothermal     | 300 W Xenon Arc Lamp (λ > 420 nm); 100 mg Catalyst in 500 mL Reactor; Introducing CO₂ and H₂O Vapor by Bubbling Approach. | CO: 5.19 µmol h⁻¹ g⁻¹ | [119] |
| Bi₄TaO₆Cl /W₁₈O₄₉ | No          | Solvothermal     | 180 mW/cm² Solar Light (λ < 800 nm); 300 W Xe Lamp; 0.02 g Photocatalyst and 2 mL H₂O in Reactor; Filled with CO₂. The Reactor was Heated to 393 K. | CO: 23.42 µmol h⁻¹ g⁻¹ | [120] |
| Bi₂O₂CO₂/Bi/Bi₂WO₆ | Bi          | Solvothermal     | 0.1 g Photocatalyst and 100 mL H₂O in Reactor; CO₂ was Inflated into the Reactor (80 kPa). | CH₄: 2.54 µmol h⁻¹ g⁻¹ CO: 0.82 µmol h⁻¹ g⁻¹ | [71] |
| g-C₃N₄∥BiOBr   | Au          | Water Bath       | 0.1 g Samples were Uniformly Dispersed onto a Glass Sheet put in 350 mL Reactor; 1.3 g NaHCO₃ reacted with 5 mL H₂SO₄ (4M) to in situ Generate CO₂. 300 W Xe Arc Lamp with a UV cut-off Filter of 420 nm; 50 mg of the Catalyst was Uniformly Distributed in the Photoreactor (250 mL); A Water Bubbler to generate a Mixture of CO₂ and Water Vapor. | CH₄: 0.92 µmol h⁻¹ g⁻¹ CO: 6.67 µmol h⁻¹ g⁻¹ | [121] |
| Bi₂WO₆∥/RGO /g-C₃N₄ | No          | Hydrothermal     | 300 W Xe Arc Lamp with a UV cut-off Filter of 420 nm; 50 mg of the Catalyst was Uniformly Distributed in the Photoreactor (250 mL); A Water Bubbler to generate a Mixture of CO₂ and Water Vapor. | CH₄: 15.96 µmol h⁻¹ g⁻¹ CO: 2.51 µmol h⁻¹ g⁻¹ | [122] |
| g-C₃N₄∥Bi₂O₃I₂ | No          | Complex Precursor Method | 0.1 g Samples were Uniformly dispersed onto a Glass Sheet, put in 350 mL Reactor; NaHCO₃ reacted with 5 mL H₂SO₄ (4M) to achieve 1 atm CO₂. 300 W Xe Lamp (λ > 420 nm); | CH₄: 15.8 µmol h⁻¹ g⁻¹ CO: 2.51 µmol h⁻¹ g⁻¹ | [123] |
| BiVO₄/C/Cu₂O   | No          | SILAR            | A 1 cm² Specimen of the Sample was placed at 50 mL Reactor which charged with 5 mL of H₂O; The Reactor was purged with CO₂. | CH₄: 45.6 µmol h⁻¹ g⁻¹ CO: 3.01 µmol h⁻¹ g⁻¹ | [124] |
The CO$_2$ adsorption process can be improved by using the photocatalyst with large surface area. Modulating the morphology is an efficient way to obtain the photocatalyst with large surface area. Jung’s group reported Z-scheme BiVO$_4$/carbon-coated Cu$_2$O (BVO/C/Cu$_2$O) nanowire arrays (NWAs) with a three-dimensional (3D) structure for efficient photoconversion of CO$_2$ to CO and CH$_4$ [124]. The highest CO formation rate on this BVO/C/Cu$_2$O NWAs reached 3.01 μmol h$^{-1}$·g$^{-1}$, which is about 9.4 and 4.7 times on Cu$_2$O mesh and Cu$_2$O NWAs, respectively. The dramatically enhanced photocatalytic activity was ascribed to the construction of a Z-scheme on a 3D NWAs structure. Enlarged surface area and enhanced charge-carrier transfer of 3D NWAs structure was evidenced by the electrochemical surface area method and photocurrent experiment results, respectively. Owing to the large surface area, enhanced charge-transport property, and light scattering or reflecting effect of the 3D NWAs structure, the combination of unique 3D morphology with a Z-scheme charge flow is not only beneficial for the efficient charge separation and transfer [125], but also favorable for facilitating the light absorption and CO$_2$ adsorption by providing ample active sites [126,127]. Moreover, the thermodynamic feasibility of the photocatalytic reduction of CO$_2$ and water oxidation on this BVO/C/Cu$_2$O NWAs was verified by the band edge configuration via ultraviolet photoelectron spectroscopy. The Z-scheme charge-transfer mechanism was confirmed by investigating the energy level of the photoinduced hole via a photoluminescence (PL) experiment using coumarin as a probe molecule in water.

Apart from morphology modulation of the photocatalyst, introducing a co-catalyst in the Bi-based Z-scheme system to improve the photocatalytic CO$_2$ reduction process is another efficient way. Recently, Jo and coworkers [122] constructed a Z-scheme Bi$_2$WO$_6$/rGO/g-C$_3$N$_4$ (BWO/rGO/CN) for photocatalytic CO$_2$ reduction. Therein, rGO with excellent conductivity and large specific area was used as a co-catalyst for the Z-scheme photocatalyst to not only facilitate charge-carrier migration in Z-scheme mode, but also benefit the CO$_2$ adsorption and electron capture by establishing the unique π−π conjugation interaction and providing abundant active sites and further promoting the CO$_2$ photoreduction. In addition, attributed to forming large intimate interfaces, the 2D/2D/2D configuration of BWO/rGO/CN possesses strong light absorption in the visible region and strong electron shuttling at the interfaces hindering the direct recombination of charge carriers. As a consequence, the optimized Z-scheme BWO/rGO/CN displayed a remarkable photocatalytic performance for not only CO$_2$ reduction but also water splitting. The AQY of 0.75% at 400 nm was higher than the other state-of-the-art CO$_2$ photoreduction catalyst system.

Moreover, integrating other techniques with photocatalytic CO$_2$ reduction over a direct Z-scheme system will obtain unexpected results. The recently reported photothermal synergic enhancement of photocatalytic CO$_2$ reduction performance of a direct Z-scheme Bi$_4$TaO$_8$Cl/W$_{18}$O$_{49}$ (BiW) system is an interesting example of the integration of the photocatalytic process with external heating [120]. The direct Z-scheme heterojunction was successfully fabricated by growing W$_{18}$O$_{49}$ nanostructures on the surface of a Bi$_4$TaO$_8$Cl nanosheet (See Figure 7a). The well matched energy band of these two semiconductors makes the constructed Z-scheme heterojunction a promising photocatalyst for CO$_2$ reduction and H$_2$O oxidation under visible light. Under photothermal conditions, the CO yield of the optimal BiW was increased surprisingly by 87 times over photocatalytic conditions (see Figure 7b). Interestingly, after light irradiation, long-lasting catalytic reduction of CO$_2$ in the dark was observed. The possible reasons for these experimental results are that external heating enhances the Z-scheme behavior of the BiW heterostructure by helping electrons at electron traps detrap to the surface of photocatalyst to increase the efficiency of electron utilization and promote the CO$_2$ reduction reaction, at the same time, decreasing the activation energy of lattice oxygen to promote oxidation reactions at the other reaction sites. The photoexcited electrons stored at the oxygen vacancy defects of W$_{18}$O$_{49}$ can be released and excited to the conduction band of Bi$_4$TaO$_8$Cl by heating to reduce CO$_2$ and produce considerable CO in the dark after light irradiation (See Figure 7c). The design of this photothermal catalyst provides a novel and promising method for using solar energy to catalyze the reduction of CO$_2$ to fuels.
From Table 4, the main product of CO₂ photoreduction in most Bi-based Z-scheme systems are CO and CH₄. By comparing all the reaction equations of products from CO₂ reduction (Equations (4)–(9)), the redox potential $E^0$ of CO₂/CH₄ ($-0.24$ V vs. NHE) is the least negative value, which means the reaction of producing CH₄ is one in which a reaction occurs most easily from a thermodynamic viewpoint. The CO formation through simple two-electron reduction process of CO₂ is easier to achieve than the other products’ generation through a multiple-electron reduction process of CO₂. In order to photoreduce CO₂ to obtain more carbonaceous products via more difficult multi-electron-transfer pathways, further exploration is still needed such as with the help of a noble metal cocatalyst. Meanwhile, water usually serves as an electron donor during CO₂ photoreduction process. In ideal conditions, H₂O should be oxidized into protons and O₂ (Equation (10)). However, the generated protons actually can further react with photoexcited electrons to produce H₂ (Equation (11)). At the same time, O₂ also can react with photoexcited electrons to produce H₂O (Equation (12)). These reactions form competitive relationship with CO₂ photoreduction (Equations (4)–(9)), which makes the electron-transfer process of CO₂ photoreduction more complicate [128,129]. Therefore, to understand in depth and illuminate the actual and complicated mechanism of photocatalytic CO₂ reduction is also crucial.

$$2H^+ + 2e^- \rightarrow H_2 \quad E^0 = -0.42 \text{ V vs NHE at pH} = 7 \quad (11)$$

$$O_2 + e^- \rightarrow O_2^- \quad E_0 = -0.33 \text{ V vs NHE at pH} = 7 \quad (12)$$
3.4. Removal of Gas Phase Pollutants and Other Applications

In recent years, the emission of nitrogen oxides (NOx) from human activities into the atmosphere has become one of the major environmental problems because of the great harm of NOx to human health, climate, and agriculture [130]. In addition, NOx mainly composed of NO and NO2 can produce secondary aerosols and cause more serious environmental problems, such as acid rain, haze, photochemical smog, PM 2.5 (fine particulate matter with less than 2.5 μm diameter), and ozone accumulation, etc. [131,132]. Among various methods for NOx removal, such as physical adsorption [133], biofiltration [134], and thermal catalytic reduction [135], photocatalysis, as a green chemical method, is considered to be a promising strategy due to its high efficiency and low cost. It has been reported that Bi-based Z-scheme heterojunction systems exhibit high photocatalytic activity for pollutant removal including NOx removal because of the abundant active radicals with strong redox ability in these systems.

Zhu et al. [136] prepared a two-dimensional/two-dimensional (2D/2D) direct Z-scheme photocatalyst Bi2O2CO3/Bi4O5Br2 (BOC/BOB) by a simple one-pot hydrothermal method. The X-band electron spin resonance (ESR) spectra of O2− and OH radicals and the Fermi level calculations strongly substantiated the direct Z-scheme charge separation mechanism of 2D/2D BOC/BOB. Under simulated solar light illumination, the optimizing BOC/BOB exhibited a significantly higher photocatalytic activity (53.2%) for NOx removal than that of single-phase BOC (20.4%) and BOB (37.9%). Such improved photocatalytic activity was mainly attributed to the enhanced charge carriers’ separation efficiency and strong redox activity of remaining photogenerated charge carriers of a direct Z-scheme mode at the BOC/BOB interface. As revealed by the results of trapping experiments and ESR tests, both O2− and OH were the major active species for photocatalytic NOx removal. Similarly, direct Z-scheme Bi2MoO6/ZnIn2S4 composite semiconductor photocatalysts were successfully constructed by a facile wet impregnation method and applied for the oxidative removal of NO with H2O2 solution injected and under visible light [73]. The optimal Bi2MoO6/ZnIn2S4 exhibited superior photocatalytic activity for NO removal, and the removal efficiency reached 84.94% in 80 min, attributed to the low rate of recombination of photogenerated charge carriers in the direct Z-scheme charge transfer mode.

Volatile organic compounds (VOCs), such as alcohols, aldehydes, ketones, alkenes, and aromatic compounds, are known to cause enormous harm to human health [137]. However, highly effective VOC elimination still remains a challenge. Photocatalytic degradation is found to be an attractive and promising technique for the abatement of VOC because of its mild operation conditions (room temperature and atmospheric pressure), highly effective and thorough degradation, and good solar energy utilization capacity. Photocatalyst is one of the keys of this technique. Z-scheme photocatalysts with high specific surface area have been accepted as rational photocatalysts for photocatalytic degradation of VOCs. For example, it was shown that direct Z-scheme BiVO4/g-C3N4 with coral-like structure achieved efficient mineralization of toluene under visible light illumination [138]. Brunauer–Emmett–Teller (BET) measurement provided evidence for the high specific surface area of the coral-like structure which provides more active sites for the photocatalytic oxidation toluene. According to the results of the ESR and terephthalic acid photoluminescence (TA-PL), the enhanced photocatalytic performance of BiVO4/g-C3N4 was attributed to a direct Z-scheme migration. The degradation rate constant of the optimal BiVO4/g-C3N4 for toluene degradation reached 0.138 h−1.

As a newly developed sensing technique, photoelectrochemical (PEC) sensors have attracted tremendous attention. Such PEC sensors combine the advantages of optical detection and electrochemical detection and improve their inherent defects at the same time. Owing to a detached excitation system and detection system, the PEC has high sensitivity, rapid measurement speed, and a low background signal. Additionally, in comparison to optical detection methods with costly optical imaging system and complicated image analysis software, the cost of PEC with a simple electrochemical detection system is much lower. From the sensing mechanism of PEC, the semiconductor as photoelectrode which is excited by light to generate hole-electron pairs and further produce
The optimal I–BiOCl photoelectrode to construct a "signal-off" photocurrent signal with the separation and migration of charge carriers is the core component of PEC. However, fast recombination of photogenerated electrons and holes as one of the inherent limitations of semiconductors is a big challenge for PEC sensors. The Z-scheme charge-carrier migration mode is beneficial to the charge separation and migration as well as improving the photoelectric conversion and signal generation efficiency of PEC. For instance, a Z-scheme iodine doped BiOCl/nitrogen-doped graphene quantum dots (I–BiOCl/N–GQDs) heterojunction was prepared by a one-pot precipitation method at room temperature [139]. Such a Z-scheme I–BiOCl/N–GQDs heterojunction was used as a photoelectrode to construct a “signal-off” cathodic PEC sensor for the selective detection of chlorpyrifos. The optimal I–BiOCl/N–GQDs composite exhibited the highest photocurrent signal (See Figure 8a) indicating excellent spatial separation efficiency of charge carriers which was evidenced by PL and EIS results. The Z-scheme charge carrier transfer pathway and the enhanced light harvesting can be used to explain the improved PEC performance. Figure 8b displays the PEC detection mechanism of chlorpyrifos. As shown in Figure 8b, in the presence of chlorpyrifos in the solution, the S and N atoms of chlorpyrifos will bind with the Bi(III) to form the bismuth-chlorpyrifos complex on the surface of I–BiOCl/N–GQDs, which will decrease the photocurrent signal because of the steric hindrance effect to achieve detection of chlorpyrifos. As shown in Figure 8c,d, this PEC sensor presented a wide linear detection range (0.3–80 ng·mL⁻¹), considerably low detection limit (0.01 ng·mL⁻¹), and good selectivity toward chlorpyrifos. Nevertheless, there is a lack of evidence for verifying the Z-scheme charge carrier transfer pathways in this work.

Figure 8. (a) Transient photocurrent of different photocatalysts (a: BiOCl, b: BiOI, c: I–BiOCl, d–f: I–BiOCl/N–GQDs-x (x: the volume of nitrogen-doped graphene quantum dots (N–GQDs), x = 0.5, 1.0, 1.5)); (b) schematic diagram of the “signal-off” cathodic PEC sensor constructed by I–BiOCl/N–GQDs for selective detection of chlorpyrifos; (c) Photocurrent response of I–BiOCl/N–GQDs-0.5 in the presence of 0 ng·mL⁻¹, 0.3 ng·mL⁻¹, 0.5 ng·mL⁻¹, 4 ng·mL⁻¹, 10 ng·mL⁻¹, 20 ng·mL⁻¹, 30 ng·mL⁻¹, 40 ng·mL⁻¹, 50 ng·mL⁻¹, 60 ng·mL⁻¹, 70 ng·mL⁻¹, 80 ng·mL⁻¹ chlorpyrifos (from a to l); Insert is the corresponding linear relationship between the log $C_{\text{chlorpyrifos}}$, and photocurrent. (d) PEC response of I–BiOCl/N–GQDs-0.5 to chlorpyrifos and other foreign impurities. Reprinted with permission from [139]. Copyright ACS, 2018.
4. Conclusions and Perspectives

As one of the most promising light-conversion technologies, photocatalysis can ease the problem of energy and environmental pollution in the future by using appropriate semiconductor as photocatalysts and solar energy as energy input to drive photocatalytic reactions. Photocatalysts are a crucial factor which determine the performance of this technique. Bi-based semiconductors with advantages of non-toxicity, low cost and good thermal stability and as a new and important visible light-activated semiconductor have attracted great attention and become a research hotspot. Recently, great progress has been made in improving the visible-light absorption ability, light-harvesting efficiency, and photogenerated carriers’ separation of Bi-based semiconductors. However, for a single-component Bi-based semiconductor, it is hard to simultaneously satisfy strong redox ability for a specific photocatalytic reaction and the good solar energy utilization capacity. Z-scheme heterojunction construction is considered a promising strategy to conquer this conflict via combining a narrow bandgap semiconductor and one or more paired semiconductor with appropriate energy band structure to broaden the light response range and enhance the redox ability of photocatalyst composite. Bi-based Z-scheme photocatalysts exhibit good performance in various photocatalytic applications involving energy production, for example, water splitting, environmental remediation such as CO$_2$ reduction, NO$_x$ removal, pollutants degradation, as well as pollutant detection, for example, construction of PEC sensors.

However, the study of the Bi-based Z-scheme heterojunction is still in its infancy and has many challenges and problems: (1) selecting two or more semiconductors with good matched band structure is the prerequisite for the successful preparation of direct Z-scheme photocatalysts. Moreover, the selected semiconductor components should satisfy the requirement that one of two contacted semiconductors should have higher CB, VB position and $E_f$ than the other, whereas whether the constructed photocatalyst follows the direct Z-scheme mechanism or not can be validated by the experimental methods performing expensive instruments. Therefore, the combination theoretical calculation and simulation with experimental characterizations may be a cost-effective strategy to comprehensively understanding the mechanism of Z-scheme and successfully construct direct Z-sheme photocatalysts. (2) Optimizing and controlling the contact interface between the selected semiconductor components of a direct Z-scheme photocatalyst is necessary for high efficiency of charge carrier separation and transfer which is beneficial to enhance the photocatalytic performance of prepared direct Z-scheme photocatalysts. (3) For specific photocatalytic applications, introducing suitable, abundant, and inexpensive co-catalysts into the Bi-based Z-scheme semiconductor will further improve the efficiency of photocatalytic applications. In addition, modulating the morphology of the Bi-based Z-scheme semiconductor to obtain high specific surface area is another way to enhance the efficiency of photocatalytic applications owing to this providing more active sites for the reactive matters. (4) In practical applications, it is also necessary to consider the recovery of Bi-based Z-scheme photocatalysts. In most applications, the photocatalyst is dispersed in the solution in the form of powders, which makes recovery work after application very complicated. Thus, constructing Bi-based Z-scheme photocatalysts with magnetic or self-floating properties is a new direction.

Owing to the potential of the Bi-based Z-scheme photocatalyst, it would be promising to realize its industrialization after resolving these challenges.

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References

1. Xiang, Q.J.; Cheng, B.; Yu, J.G. Graphene-Based Photocatalysts for Solar-Fuel Generation. Angew. Rev. 2015, 54, 11350–11360. [CrossRef] [PubMed]
2. Hu, L.L.; Liao, Y.H.; Xia, D.H.; Zhang, Q.; He, H.J.W.; Yang, J.L.; Huang, Y.J.; Liu, H.D.; Zhang, F.; He, C.; et al. In-situ fabrication of AgI-BiO nanoarrays film photoelectrode for efficient wastewater treatment, electricity production and enhanced recovery of copper in photocatalytic fuel cell. Catal. Today 2020, 339, 379–390. [CrossRef]
3. Berglund, S.P.; Abdi, F.F.; Bogdanoff, P.; Chemseddine, A.; Friedrich, D.; van de Krol, R. Comprehensive Evaluation of CuBiO as a Photocathode Material for Photoelectrochemical Water Splitting. Chem. Mater. 2016, 28, 4231–4242. [CrossRef]
4. Liu, A.J.; Zhu, Y.C.; Li, K.Z.; Chu, D.M.; Huang, J.; Li, X.; Zhang, C.Y.; Yang, P.; Du, Y.K. A high performance p-type nickel oxide/cuprous oxide nanocomposite with heterojunction as the photoanodic catalyst for water splitting to produce hydrogen. Chem. Phys. Lett. 2018, 703, 56–62. [CrossRef]
5. Hampel, B.; Pap, Z.; Sapi, A.; Szamosvolgyi, A.; Baia, L.; Hernadi, K. Application of TiO2–Cu Composites in Photocatalytic Degradation Different Pollutants and Hydrogen Production. Catalysts 2020, 10, 85. [CrossRef]
6. Sun, N.; Qu, Y.; Yang, C.H.; Yang, Z.D.; Yan, R.; Wenyu, E.; Zhang, Z.Q.; Li, Z.J.; Li, H.N.; Khan, I.; et al. Efficient photocatalytic degradation of monochlorophenol on in-situ fabricated BiPOO/β-BiO3 heterojunction microspheres and O2-free hole-induced selective dechloridation conversion with H2 evolution. Appl. Catal. B Environ. 2020, 263, 118313. [CrossRef]
7. Yamashita, H.; Fujiwara, S.; Inoue, K.; Park, D.R.; Koyano, K.; Tatsumi, T.; Anpo, M. Selective formation of CH3OH in the photocatalytic reduction of CO2 with H2O on titanium oxides highly dispersed within zeolites and mesoporous molecular sieves. Catal. Today 1998, 45, 221–227. [CrossRef]
8. Dakhshinamoorthy, A.; Navalon, S.; Corma, A.; Garcia, H. Photocatalytic CO2 reduction by TiO2 and related titanium containing solids. Energy Environ. Sci. 2012, 5, 9217–9233. [CrossRef]
9. Kondo, Y.; Yoshikawa, H.; Awaga, K.; Murayama, M.; Mori, T.; Sunaka, K.; Bandow, S.; Iijima, S. Preparation, Photocatalytic Activities, and Dye-Sensitized Solar-Cell Performance of Submicron-Scale TiO2 Hollow Spheres. Langmuir 2008, 24, 547–550. [CrossRef] [PubMed]
10. Sun, W.T.; Yu, A.; Pan, H.Y.; Gao, X.F.; Chen, Q.; Peng, L.M. CdS quantum dots sensitized TiO2 nanotube-array photoelectrodes. J. Am. Chem. Soc. 2009, 130, 1124–1125. [CrossRef] [PubMed]
11. Fu, J.W.; Zhu, B.C.; Jiang, C.J.; Cheng, B.; You, W.; Yu, J.G. Hierarchical Porous O-Doped g-C3N4 with Enhanced Photocatalytic CO2 Reduction Activity. Small 2017, 13, 1603938. [CrossRef]
12. Sorcar, S.; Hwang, Y.; Grimes, C.A.; In, S.-I. Highly enhanced and stable activity of defect-induced titania nanoparticles for solar light-driven CO2 reduction into CH4. Mater. Today 2017, 20, 507–515. [CrossRef]
13. Xu, M.; Zada, A.; Rui, Y.; Li, H.N.; Sun, N.; Qu, Y. Ti3O5/TiO2 heterophase junction with enhanced charge separation and spatially separated active sites for photocatalytic CO2 reduction. Phys. Chem. Chem. Phys. 2020, 22, 4526–4532. [CrossRef]
14. Chen, F.; Ma, Z.Y.; Ye, L.Q.; Ma, T.Y.; Zhang, T.R.; Zhang, Y.; Hu, H.W. Macroscopic Spontaneous Polarization and Surface Oxygen Vacancies Collaboratively Boosting CO2 Photoreduction on BiOIO3 Single Crystals. Adv. Mater. 2020, 32, 1908350. [CrossRef]
15. Jin, J.P.; Chen, S.T.; Wang, J.M.; Chen, C.; Peng, T.Y. One-pot hydrothermal preparation of PbO-decorated brookite/anatase TiO2 composites with remarkably enhanced CO2 photoreduction activity. Appl. Catal. B Environ. 2020, 263, 118353. [CrossRef]
16. Najafian, H.; Manteghi, F.; Beshkar, F.; Salavati-Niasari, M. Fabrication of nanocomposite photocatalyst CuBi2O4/Bi3ClO4 for removal of acid brown 14 as water pollutant under visible light irradiation. J. Hazard. Mater. 2019, 361, 210–220. [CrossRef]

17. Liu, S.; Zhao, M.Y.; He, Z.T.; Zhong, Y.; Ding, H.; Chen, D.M. Preparation of a p-n heterojunction 2D BiOI nanosheet/1DBiPO4 nanorod composite electrode for enhanced visible light photoelectrocatalysis. Chin. J. Catal. 2019, 40, 446–457. [CrossRef]

18. Li, W.F.; Yu, R.; Li, M.; Guo, N.; Yu, H.W.; Yu, Y. Photocatalytical degradation of diclofenac by Ag-BiOI-rGO: Kinetics, mechanisms and pathways. Chemosphere 2019, 218, 966–973. [CrossRef]

19. Guo, F.; Li, M.Y.; Ren, H.J.; Huang, X.L.; Hou, W.X.; Wang, C.; Shi, W.L.; Lu, C.Y. Fabrication of p-n CuBi2O4/MoS2 heterojunction with nanosheets-on-microrods structure for enhanced photocatalytic activity towards tetracycline degradation. Appl. Surf. Sci. 2019, 491, 88–94. [CrossRef]

20. Soltani, T.; Tayyebi, A.; Lee, B.-K. BiFeO3/BiVO4 p-n heterojunction for efficient and stable photocatalytic and photoelectrochemical water splitting under visible-light irradiation. Catal. Today 2020, 340, 188–196. [CrossRef]

21. Li, X.W.; Zhang, W.D.; Li, J.Y.; Jiang, G.M.; Zhou, Y.; Lee, S.C.; Dong, F. Transformation pathway and toxic intermediates inhibition of photocatalytic NO removal on designed Bi metal@defective Bi2O2SiO3. Appl. Catal. B Environ. 2019, 241, 187–195. [CrossRef]

22. Wang, L.; Xu, K.; Cui, W.; Lv, D.D.; Wang, L.; Ren, L.; Xu, X.; Dong, F.; Dou, S.X.; Hao, W.C.; et al. Monolayer Epitaxial Heterostructures for Selective Visible-Light-Driven Photocatalytic NO Oxidation. Adv. Funct. Mater. 2019, 29, 1808084. [CrossRef]

23. Carbonaro, S.; Sugihara, M.N.; Strathmann, T.J. Continuous-flow photocatalytic treatment of pharmaceutical micropollutants: Activity, inhibition, and deactivation of TiO2 photocatalysts in wastewater effluent. Appl. Catal. B Environ. 2013, 129, 1–12. [CrossRef]

24. Bai, S.; Jiang, J.; Zhang, Q.; Xiong, Y.J. Steering charge kinetics in photocatalysis: Intersection of materials syntheses, characterization techniques and theoretical simulations. Chem. Soc. Rev. 2015, 44, 2893–2939. [CrossRef]

25. Fujishima, A.; Kenichi, H. Electrochemical photolysis of water at a semiconductor electrode. Nature 1972, 238, 37–38. [CrossRef]

26. Sohn, Y.; Huang, WX.; Taghipour, F. Recent progress and perspectives in the photocatalytic CO2 reduction of Ti-oxide-based nanomaterials. Appl. Surf. Sci. 2017, 396, 1696–1711. [CrossRef]

27. Joo, J.B.; Zhang, Q.; Dahl, M.; Lee, I.; Goebel, J.; Zaera, F.; Yin, Y.D. Control of the nanoscale crystallinity in mesoporous TiO2 shells for enhanced photocatalytic activity. Energy Environ. Sci. 2012, 5, 6321–6327. [CrossRef]
35. Qian, R.F.; Zong, H.X.; Schneider, J.; Zhou, G.D.; Zhao, T.; Li, Y.L.; Yang, J.; Bahnemann, D.W.; Pan, J.H. Charge carrier trapping, recombination and transfer during TiO₂ photocatalysis: An overview. Catal. Today 2019, 335, 78–90. [CrossRef]

36. Negrín-Montecelo, Y.; Testa-Anta, M.; Marin-Caba, L.; Pérez-Lorenzo, M.; Salgueirinho, V.; Correa-Duarte, M.A.; Comesas-Hermo, M. Titanate Nanowires as One-Dimensional Hot Spot Generators for Broadband Au–TiO₂ Photocatalysis. Nanomaterials 2019, 9, 990. [CrossRef]

37. Nogueira, A.C.; Gomes, L.E.; Ferencz, J.A.P.; Rodrigues, J.E.F.S.; Gonçalves, R.V.; Wender, H. Improved Visible Light Photoactivity of Cu₆Bi₄O₁₂/CuO Heterojunctions for Photodegradation of Methylene Blue and Metronidazole. J. Phys. Chem. C 2019, 123, 25680–25690. [CrossRef]

38. Hu, J.Y.; Zhai, C.Y.; Gao, H.F.; Zeng, L.X.; Du, Y.K.; Zhu, M.S. Enhanced photo-assisted ethanol electro-oxidation activity by using broadband visible light absorption of a graphitic C₃N₄/BiOI carrier. Sustain. Energy Fuels 2019, 3, 439–449. [CrossRef]

39. Liu, H.H.; Yang, C.; Huang, J.; Chen, J.F.; Zhong, J.B.; Li, J.Z. Ionic liquid-assisted hydrothermal preparation of BiOI/BiOCl heterojunctions with enhanced separation efficiency of photo-generated charge pairs and photocatalytic performance. Inorg. Chem. Commun. 2020, 113, 107806. [CrossRef]

40. Samran, B.; Lunput, S.; Tonnonchiang, S.; Chaiwichian, S. BiFeO₃/BiVO₄ nanocomposite photocatalysts with highly enhanced photocatalytic activity for rhodamine B degradation under visible light irradiation. Phys. B Condens. Matter 2019, 561, 23–28. [CrossRef]

41. Lim, H.; Rawal, S.B. Integrated Bi₂O₃ nanostructure modified with Au nanoparticles for enhanced photocatalytic activity under visible light irradiation. Prog. Nat. Sci. Mater. Int. 2017, 27, 289–296. [CrossRef]

42. Zhao, G.Q.; Zheng, Y.J.; He, Z.G.; Lu, Z.X.; Wang, L.; Li, C.F.; Jiao, F.P.; Deng, C.Y. Synthesis of Bi₂S₃ microsphere and its efficient photocatalytic activity under visible-light irradiation. Trans. Nonferrous Met. Soc. China 2018, 28, 2002–2010. [CrossRef]

43. Shi, H.X.; Fan, J.; Zhao, Y.Y.; Hu, X.Y.; Zhang, X.; Tang, Z.S. Visible light driven Cu₆Bi₄O₁₂/Bi₂MoO₆ p-n heterojunction with enhanced photocatalytic inactivation of E. coli and mechanism insight. J. Hazard. Mater. 2020, 381, 121006. [CrossRef]

44. Qiu, F.Z.; Li, W.Z.; Wang, F.Z.; Li, H.D.; Liu, X.T.; Ren, C.J. Preparation of novel p-n heterojunction Bi₂O₂CO₃/BiOBr photocatalysts with enhanced visible light photocatalytic activity. Colloids Surf. A Physicochem. Eng. Asp. 2017, 517, 25–32. [CrossRef]

45. Liu, D.; Cai, W.B.; Wang, Y.G.; Zhu, Y.F. Constructing a novel Bi₃SiO₅/BiPO₄ heterostructure with extended light response range and enhanced photocatalytic performance. Appl. Catal. B Environ. 2018, 236, 205–211. [CrossRef]

46. Li, S.J.; Hu, S.W.; Jiang, W.; Liu, Y.; Liu, J.S.; Wang, Z.H. Facile synthesis of flower-like Ag₃VO₄/Bi₅W₈O₂₆ heterojunction with enhanced visible-light photocatalytic activity. J. Colloid Interface Sci. 2017, 501, 156–163. [CrossRef]

47. Zhang, K.; Liu, C.; Huang, F.; Zheng, C.; Wang, W. Study of the electronic structure and photocatalytic activity of the BiOCl photocatalyst. Appl. Catal. B Environ. 2006, 68, 125–129. [CrossRef]

48. He, R.A.; Cao, S.W.; Zhou, P.; Yu, J.G. Recent advances in visible light Bi-based photocatalysts. Chin. J. Catal. 2014, 35, 989–1007. [CrossRef]

49. Zeng, L.; Zhe, F.; Wang, Y.; Zhang, Q.L.; Zhao, X.Y.; Hu, X.; Wu, Y.; He, Y.M. Preparation of interstitial carbon doped BiOI for enhanced performance in photocatalytic nitrogen fixation and methyl orange degradation. J. Colloid Interface Sci. 2019, 539, 563–574. [CrossRef]

50. Tian, F.; Li, G.F.; Zhao, H.P.; Chen, F.X.; Li, M.; Liu, Y.L.; Chen, R. Residual Fe enhances the activity of BiOCl hierarchical nanostructure for hydrogen peroxide activation. J. Catal. 2019, 370, 265–273. [CrossRef]

51. Liu, Y.; Hu, Z.F.; Yu, J.C. Fe Enhanced Visible-Light-Driven Nitrogen Fixation on BiOBr Nanosheets. Chem. Mater. 2020, 32, 1488–1494. [CrossRef]

52. Kim, J.H.; Lee, J.S. Elaborately Modified BiVO₄ Photoanodes for Solar Water Splitting. Adv. Mater. 2019, 31, 1806938. [CrossRef] [PubMed]

53. Hao, Q.; Wang, R.T.; Lu, H.J.; Xie, C.A.; Ao, W.H.; Chen, D.M.; Ma, C.; Yao, W.Q.; Zhu, Y.F. One-pot synthesis of C/Bi₂O₃ composite with enhanced photocatalytic activity. Appl. Catal. B Environ. 2017, 219, 63–72. [CrossRef]
54. Ge, Z.H.; Qin, P.; He, D.S.; Chong, X.; Feng, D.; Ji, Y.H.; Feng, J.; He, J.Q. Highly Enhanced Thermoelectric Properties of Bi/Bi2S3 Nanocomposites. *Appl. Mater. Interfaces* **2017**, *9*, 4828–4834. [CrossRef]

55. Xu, W.C.; Fang, J.Z.; Chen, Y.F.; Lu, S.Y.; Zhou, G.Y.; Zhu, X.M.; Fang, Z.Q. Novel heterostructured Bi2S3/Bi2S3O2 with highly visible light photocatalytic activity for the removal of rhodamine B. *Mater. Chem. Phys.* **2015**, *154*, 30–37. [CrossRef]

56. Guo, J.H.; Shi, L.; Zhao, J.Y.; Ying, Y.; Tang, K.B.; Zhang, W.Q.; Xie, C.Z.; Yuan, X.Y. Enhanced visible-light photocatalytic activity of Bi2MoO6 nanolayers with heterogeneous Bi2MoO6@Bi2MoO6 core-shell structure. *Appl. Catal. B Environ.* **2018**, 224, 692–704. [CrossRef]

57. He, R.G.; Xu, D.F.; Cheng, B.; Yu, J.G.; Ho, W. A review on nanoscale Bi-based photocatalysts. *Nanoscale Horiz.* **2018**, 3, 464–504. [CrossRef]

58. Qi, K.Z.; Cheng, B.; Yu, J.G.; Ho, W. A review on TiO2-based Z-scheme photocatalysts. *Chin. J. Catal.* **2017**, 38, 1936–1955. [CrossRef]

59. Xu, Q.; Zhang, L.Y.; Yu, J.G.; Wageh, S.; Al-Ghamdi, A.A.; Jaroniec, M. Direct Z-scheme photocatalysts: Principles, synthesis, and applications. *Mater. Today* **2018**, 21, 1042–1063. [CrossRef]

60. Zhang, L.; Xu, T.; Zhao, X.; Zhu, Y. Controllable synthesis of Bi2MoO6 and effect of morphology and variation in local structure on photocatalytic. *Appl. Catal. B Environ.* **2010**, 98, 138–146. [CrossRef]

61. Ding, L.; Wei, R.; Chen, H.; Hu, J.; Li, J. Controllable synthesis of highly active BiOCl hierarchical microsphere self-assembled by nanosheets with tunable thickness. *Appl. Catal. B Environ.* **2015**, 172, 91–99. [CrossRef]

62. Zhou, L.; Wang, W.Z.; Xu, H.L.; Sun, S.M.; Shang, M. Bi2O3 Hierarchical Nanostructures: Controllable Synthesis, Growth Mechanism, and their Application in Photocatalysis. *Chem. A Eur. J.* **2009**, 15, 1776–1782. [CrossRef] [PubMed]

63. Ye, R.Q.; Fang, H.B.; Zheng, Y.Z.; Li, N.; Wang, Y.; Tao, X. Fabrication of CoTiO3/g-C3N4 Hybrid Photocatalysts with Enhanced H2 Evolution: Z-Scheme Photocatalytic Mechanism Insight. *ACS Appl. Mater. Interfaces* **2016**, 8, 13879–13889. [CrossRef]

64. Li, Y.S.; Li, J.; Li, J.G. Metal/semiconductor Nanocomposites for Photocatalysis: Fundamentals, Structures, Applications and Properties. *Nanomaterials* **2019**, 9, 359. [CrossRef]

65. Nie, N.; Zhang, L.Y.; Fu, J.W.; Cheng, B.; Yu, J.G. Self-assembled hierarchical direct Z-scheme g-C3N4/ZnO microspheres with enhanced photocatalytic CO2 reduction performance. *Appl. Surf. Sci.* **2018**, 441, 12–22. [CrossRef]

66. Zhang, C.L.; Yu, S.H. Nanoparticles meet electrospinning: Recent advances and future prospects. *Chem. Soc. Rev.* **2014**, 43, 4423. [CrossRef]

67. Ali, R.; Ma, M.; Kim, S.; Shah, M.S.A.S.; Chung, C.; Park, J.H.; Yoo, P.J. Mediator and Co-Catalysts-Free Direct Z-Scheme Composites of Bi2WO6–Cu2P for Solar-Water Splitting. *Nanoscale* **2018**, 10, 3026–3036. [CrossRef]

68. Rivest, J.B.; Jain, P.K. Cation exchange on the nanoscale: An emerging technique for new material synthesis, device fabrication, and chemical sensing. *Chem. Soc. Rev.* **2013**, 42, 89–96. [CrossRef]

69. Yuan, X.J.; Shen, D.Y.; Zhang, Q.; Zou, H.B.; Liu, Z.L.; Peng, F. Z-scheme Bi2WO6/CuBI2O4 heterojunction mediated by interfacial electric field for efficient visible-light photocatalytic degradation of tetracycline. *Chem. Eng. J.* **2019**, 369, 292–301. [CrossRef]

70. Zhang, Y.Y.; Wang, L.L.; Dong, F.Y.; Chen, Q.; Jiang, H.Y.; Xu, M.; Shi, J.S. Non-additional carbon source one-step synthesis of Bi2O3CO2-based ternary composite for efficient Z-scheme photocatalysis. *J. Colloid Interface Sci.* **2019**, 536, 575–585. [CrossRef]

71. Wang, H.; Ye, H.L.; Zhang, B.H.; Zhao, F.Q.; Zeng, B.Z. Electrostatic interaction mechanism based synthesis of a Z-scheme BiO1–CdS photocatalyst for selective and sensitive detection of Cu2+. *J. Mater. Chem. A* **2017**, 5, 10599–10608. [CrossRef]

72. Wan, S.P.; Zhong, Q.; Ou, M.; Zhang, S.L. Synthesis and characterization of direct Z-scheme Bi2MoO6/ZnIn2S4 composite photocatalyst with enhanced photocatalytic oxidation of NO under visible light. *J. Mater. Sci.* **2017**, 52, 11453–11466. [CrossRef]

73. Li, B.S.; Lai, C.; Zeng, G.M.; Qin, L.; Yi, H.; Huang, D.L.; Zhou, C.Y.; Liu, X.G.; Cheng, M.; Xu, P.; et al. Facile Hydrothermal Synthesis of Z-Scheme Bi2FeO4@Bi2WO6 Heterojunction Photocatalyst with Enhanced Visible Light Photocatalytic Activity. *ACS Appl. Mater. Interfaces* **2018**, 10, 18824–18836. [CrossRef] [PubMed]
75. Che, H.N.; Che, G.B.; Jiang, E.H.; Liu, C.B.; Dong, H.J.; Li, C.M. A novel Z-Scheme CdS/BiOCl heterostructure for photocatalytic degradation of antibiotics: Mineralization activity, degradation pathways and mechanism insight. *J. Taiwan Inst. Chem. Eng.* 2018, 91, 224–234. [CrossRef]

76. He, R.A.; Zhou, J.Q.; Fu, H.Q.; Zhang, S.Y.; Jiang, C.J. Room-temperature in situ fabrication of Bi2O3/g-C3N4 direct Z-scheme photocatalyst with enhanced photocatalytic activity. *Appl. Surf. Sci.* 2018, 430, 273–282. [CrossRef]

77. Song, C.J.; Feng, Y.; Shi, W.D.; Liu, C.B. Fabrication and mechanism of a novel direct solid-state Z-scheme photocatalyst CdS/BiOI under visible light. *CryEngComm* 2016, 18, 7796–7804. [CrossRef]

78. Wang, S.Y.; Yang, X.L.; Zhang, X.H.; Ding, X.; Yang, Z.X.; Dai, K.; Chen, H. A plate-on-plate sandwiched Z-scheme heterojunction photocatalyst: BiOBr-Bi2MoO6 with enhanced photocatalytic performance. *Appl. Surf. Sci.* 2017, 391, 194–201. [CrossRef]

79. Zhang, J.F.; Hu, Y.F.; Jiang, X.L.; Chen, S.F.; Meng, S.G.; Fu, X.L. Design of a direct Z-scheme photocatalyst: Preparation and characterization of Bi2O3/g-C3N4 with high visible light activity. *J. Hazard. Mater.* 2014, 280, 713–722. [CrossRef]

80. Cui, M.; Yu, J.X.; Lin, H.J.; Wu, Y.; Zhao, L.H.; He, Y.M. In-situ preparation of Z-scheme AgI/Bi2O3-I hybrid and its excellent photocatalytic activity. *Appl. Surf. Sci.* 2016, 387, 912–920. [CrossRef]

81. Xue, W.J.; Peng, Z.W.; Huang, D.L.; Zeng, G.M.; Wen, X.J.; Deng, R.; Yang, Y.; Yan, X.L. In situ synthesis of visible-light-driven Z-scheme AgI/Bi2MoO6 heterojunction photocatalysts with enhanced photocatalytic activity. *Ceram. Int.* 2019, 45, 6340–6349. [CrossRef]

82. Guo, F.; Shi, W.L.; Wang, H.B.; Han, M.M.; Guan, W.S.; Huang, H.; Liu, Y.; Kang, Z.H. Study on highly enhanced photocatalytic tetracycline degradation of type II AgI/CuBi2O4 and Z-scheme AgBr/CuBi2O4 heterojunction photocatalysts. *J. Hazard. Mater.* 2018, 349, 111–118. [CrossRef]

83. Hu, K.; Chen, C.Y.; Zhu, Y.; Zeng, G.M.; Huang, B.B.; Chen, W.Q.; Liu, S.H.; Lei, C.; Li, B.S.; Yang, Y. Ternary Z-scheme heterojunction of Bi2WO6 with reduced graphene oxide (rGO) and meso-tetra (4-carboxyphenyl) porphyrin (TCPP) for enhanced visible-light photocatalysis. *J. Colloid Interface Sci.* 2019, 540, 115–125. [CrossRef]

84. Shi, W.L.; Guo, F.; Yuan, S.L. In situ synthesis of Z-scheme Ag3PO4/CuBi2O4 photocatalysts and enhanced photocatalytic performance for the degradation of tetracycline under visible light irradiation. *Appl. Catal. B Environ.* 2017, 209, 720–728. [CrossRef]

85. Zhang, J.F.; Fu, J.W.; Wang, Z.L.; Cheng, B.; Dai, K.; Ho, W. Direct Z-scheme porous g-C3N4/BiOI heterojunction for enhanced visible-light photocatalytic activity. *J. Alloy Compd.* 2018, 766, 841–850. [CrossRef]

86. Xia, Y.M.; He, Z.M.; Su, J.B.; Tang, B.; Liu, Y. Enhanced photocatalytic performance of Z-scheme Cu2O/Bi2O3-I nanocomposites. *J. Mater. Sci. Mater. Electron.* 2018, 29, 15271–15281. [CrossRef]

87. Lu, X.Y.; Che, W.J.; Hu, X.F.; Wang, Y.; Zhang, A.T.; Deng, F.; Luo, S.L.; Dionysiou, D.D. The facile fabrication of novel visible-light-driven Z-scheme CuInS2/Bi2WO6 heterojunction with intimate interface contact by in situ hydrothermal growth strategy for extraordinary photocatalytic performance. *Chem. Eng. J.* 2019, 356, 819–829. [CrossRef]

88. Jiang, T.G.; Wang, K.; Guo, T.; Wu, X.Y.; Zhang, G.K. Fabrication of Z-scheme MoO3/Bi2O4 heterojunction photocatalyst with enhanced photocatalytic performance under visible light irradiation. *Chin. J. Catal.* 2020, 41, 161–169. [CrossRef]

89. Qin, H.M.; Wang, K.; Jiang, L.S.; Li, J.; Wu, X.Y.; Zhang, G.K. Ultrasonic-assisted fabrication of a direct Z-scheme BiOBr/Bi2O3 heterojunction with superior visible light-responsive photocatalytic performance. *J. Alloy Compd.* 2020, 821, 153417. [CrossRef]

90. Yang, Q.; Guo, E.; Liu, H.; Lu, Q.F. Engineering of Z-scheme 2D/3D architectures with Bi2MoO6 on TiO2 nanosphere for enhanced photocatalytic 4-nitrophenol degradation. *J. Taiwan Inst. Chem. Eng.* 2019, 105, 65–74. [CrossRef]

91. Guo, W.; Fan, K.; Zhang, J.J.; Xu, C.J. 2D/2D Z-scheme Bi2WO6/Porous-g-C3N4 with synergy of adsorption and visible-light-driven photodegradation. *Appl. Surf. Sci.* 2018, 447, 125–134. [CrossRef]

92. Chen, J.F.; Hu, C.; Deng, Z.; Gong, X.; Su, Y.; Yang, Q.; Zhong, J.B.; Li, J.Z.; Duan, R. Insight into visible light-driven photocatalytic performance of direct Z-scheme Bi2WO6/BiOI composites constructed in-situ. *Chem. Phys. Lett.* 2019, 716, 134–141. [CrossRef]
93. Wang, Z.L.; Hu, T.P.; Dai, K.; Zhang, J.F.; Liang, C.H. Construction of Z-scheme Ag3PO4/Bi2WO6 composite with excellent visible-light photodegradation activity for removal of organic contaminants. *Chin. J. Catal.* 2017, 38, 2021–2029. [CrossRef]

94. Li, Z.L.; Jin, C.Y.; Wang, M.; Kang, J.; Wu, Z.M.; Yang, D.E.; Zhu, T. Novel rugby-like g-C3N4/BiVO4 core/shell Z-scheme composites prepared via low-temperature hydrothermal method for enhanced photocatalytic performance. *Sep. Purif. Technol.* 2020, 232, 115937. [CrossRef]

95. Joy, J.; Mathew, J.; George, S.C. Nanomaterials for photoelectrochemical water splitting—Review. *Int. J. Hydrogen Energy* 2018, 43, 4804–4817. [CrossRef]

96. Shen, H.Q.; Liu, G.W.; Zhao, Y.; Li, D.; Jiang, J.H.; Ding, J.; Qamar, M.; Yamani, Z.H.; Byrappa, K. Ternary Bi2O3/Sb2O3Ir nanowires decorated with CdS nanoparticles as Z-scheme photocatalyst with enhanced H2 evolution. *Chem. Eng. J.* 2020, 382, 122810. [CrossRef]

97. Zhu, R.S.; Tian, F.; Yang, R.J.; He, J.S.; Zhong, J.; Chen, B.Y. Z scheme system ZnIn2S4/ZnO heterostructures for photocatalytic overall water splitting. *Appl. Catal. B Environ.* 2018, 241, 259–269. [CrossRef]

98. Sepahvand, H.; Sharifinia, S. Photocatalytic overall water splitting by Z-scheme g-C3N4/Bi2O3 heterojunction. *Int. J. Hydrog. Energy* 2020, 45, 23654–23668. [CrossRef]

99. Ma, Y.Y.; Jiang, X.; Sun, R.K.; Yang, J.L.; Jiang, X.L.; Liu, Z.Q.; Xie, M.Z.; Han, W.H. Z-scheme Bi2O3/Sb2O3Ir heterojunction nanostructures for photocatalytic overall water splitting. *Chem. Eng. J.* 2020, 382, 123020. [CrossRef]

100. Zhou, F.Q.; Fan, J.C.; Xu, Q.J.; Min, Y.L. BiVO4 nanowires decorated with CdS nanoparticles as Z-scheme photocatalyst with enhanced H2 generation. *Appl. Catal. B Environ.* 2017, 201, 77–83. [CrossRef]

101. Drmosh, Q.A.; Hezam, A.; Hendi, A.H.Y.; Qamar, M.; Yamani, Z.H.; Byrappa, K. Ternary Bi2S3/MoS2/TiO2 with double Z-scheme configuration as high performance photocatalyst. *Appl. Surf. Sci.* 2020, 499, 143938. [CrossRef]

102. Hezam, A.; Namratha, K.; Drmosh, Q.A.; Ponnamma, D.; Nagi Saeed, A.M.; Ganesh, V.; Neppolian, B.; Byrappa, K. Direct Z-scheme CS2O–Bi2O3–ZnO heterostructures for photocatalytic overall water splitting. *J. Mater. Chem. A* 2018, 6, 21379–21388. [CrossRef]

103. Zhu, R.S.; Tian, F.; Yang, R.J.; He, J.S.; Zheng, J.; Chen, B.Y. Z scheme system ZnIn2S4/RGO/BiVO4 for hydrogen generation from water splitting and simultaneous degradation of organic pollutants under visible light. *Renew. Energy* 2019, 139, 22–27. [CrossRef]

104. Shen, H.Q.; Liu, G.W.; Zhao, Y.; Li, D.; Jiang, J.H.; Ding, J.R.; Mao, B.D.; Shen, H.; Kim, K.-S.; Shi, W.D. Artificial all-solid-state system by RGO bridged Cu2O and Bi2WO6 for Z-scheme H2 production and tetracycline degradation. *Fuel* 2020, 259, 116311. [CrossRef]

105. Shen, H.Q.; Wang, M.; Zhang, X.Z.; Li, D.; Liu, G.W.; Shi, W.D. 2D/2D/2D architecture Z-scheme system for simultaneous H2 generation and antibiotic degradation. *Fuel* 2020, 280, 118618. [CrossRef]

106. Li, J.N.; Pan, Z.W.; Zhou, K.B. Enhanced photocatalytic oxygen evolution activity by formation of Ir@IrOx(OH)y core–shell heterostructure. *Nanotechnology* 2018, 29, 405705. [CrossRef]

107. Ran, J.R.; Zhang, J.; Yu, J.G.; Jaroniec, M.; Qiao, S.Z. Earth-abundant cocatalysts for semiconductor-based photocatalytic water splitting. *Chem. Soc. Rev.* 2014, 43, 7787–7812. [CrossRef]

108. Liu, Y.; Li, Y.; Peng, F.; Lin, Y.; Yang, S.Y.; Wang, H.J.; Cao, Y.H.; Yu, H. 2H– and 1T–mixed phase few-layer MoS2 as a superior to Pt co-catalyst coated on TiO2 nanorod arrays for photocatalytic hydrogen evolution. *Appl. Catal. B Environ.* 2019, 241, 236–245. [CrossRef]

109. Crake, A. Metal-organic frameworks based materials for photocatalytic CO2 reduction. *Mater. Sci. Technol.* 2017, 33, 1737–1749. [CrossRef]

110. Zhang, L.; Zhao, Z.J.; Wang, T.; Gong, J.L. Nano-designed semiconductors for electro- and photoelectro-catalytic conversion of carbon dioxide. *Chem. Soc. Rev.* 2018, 47, 5423–5443. [CrossRef] [PubMed]
114. Liu, L.J.; Li, Y. Understanding the Reaction Mechanism of Photocatalytic Reduction of CO₂ with H₂O on TiO₂-Based Photocatalysts: A Review. Aerosol Air Qual. Res. 2014, 14, 453–469. [CrossRef]

115. Wei, Z.H.; Wang, Y.F.; Li, Y.Y.; Zhang, L.; Yao, H.C.; Li, Z.J. Enhanced photocatalytic CO₂ reduction activity of Z-scheme CdS/BiVO₄ nanocomposite with thinner BiVO₄ nanosheets. J. CO₂ Util. 2018, 28, 15–25. [CrossRef]

116. Wang, J.C.; Yao, H.C.; Fan, Z.Y.; Zhang, L.; Wang, J.S.; Zang, S.Q.; Li, Z.J. 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]

117. Yuan, L.; Lu, K.Q.; Zhang, F.; Fu, X.Z.; Xu, Y.J. Unveiling the interplay between light-driven CO₂ photocatalytic reduction and carbonaceous residues decomposition: A case study of Bi₂WO₆-TiO₂ binanoshells. Appl. Catal. B Environ. 2018, 237, 424–431. [CrossRef]

118. Guo, L.N.; You, Y.; Huang, H.W.; Tian, N.; Ma, T.Y.; Zhang, Y.H. Z-scheme g-C₃N₄/TiO₂ heterojunction for enhanced photocatalytic CO₂ reduction. J. Colloid Interface Sci. 2020, 568, 139–147. [CrossRef]

119. Li, M.L.; Zhang, L.X.; Fan, X.Q.; Zhou, Y.J.; Wu, M.Y.; Shi, J.L. Highly selective CO₂ photoreduction to CO over g-C₃N₄/Bi₂WO₆ composites under visible light. J. Mater. Chem. A 2015, 3, 5189–5196. [CrossRef]

120. Yan, J.Y.; Wang, C.H.; Ma, H.; Li, Y.Y.; Liu, Y.C.; Suzuki, N.; Terashima, C.; Fujishima, A.; Zhang, X.T. Photothermal synergic enhancement of direct Z-scheme behavior of Bi₄TaO₆Cl/W₁₈O₆₉ heterostructure for CO₂ reduction. Appl. Catal. B Environ. 2020, 268, 118401. [CrossRef]

121. Bai, Y.; Chen, T.; Wang, P.Q.; Wang, L.; Ye, L.Q.; Shi, X.; Bai, W. Size-dependent role of gold in g-C₃N₄/BiOBr/Au system for photocatalytic CO₂ reduction and dye degradation. Sol. Energy Mater. Sol. Cells 2016, 157, 406–414. [CrossRef]

122. Jo, W.-K.; Kumar, S.; Eslava, S.; Tonda, S. Construction of Bi₂WO₆/RGO/g-C₃N₄ 2D/2D/2D hybrid Z-scheme heterojunctions with large interfacial contact area for efficient charge separation and high-performance photoreduction of CO₂ and H₂O into solar fuels. Appl. Catal. B Environ. 2018, 239, 586–598. [CrossRef]

123. Bai, Y.; Ye, L.; Wang, L.; Shi, X.; Wang, P.; Bai, W.; Wong, P.K. g-C₃N₄/Bi₂O₂I₂ heterojunction with I⁻/I⁻ redox mediator for enhanced photocatalytic CO₂ conversion. Appl. Catal. B Environ. 2016, 194, 98–104. [CrossRef]

124. Kim, C.; Cho, K.M.; Al-Saggaf, A.; Gereige, I.; Jung, H.T. Z-scheme Photocatalytic CO₂ Conversion on Three-Dimensional BiVO₄/Carbon-Coated Cu₂O Nanowire Arrays under Visible Light. ACS Catal. 2018, 8, 4170–4177. [CrossRef]

125. Tian, J.; Zhao, Z.H.; Kumar, A.; Boughton, R.I.; Liu, H. Recent progress in design, synthesis, and applications of one-dimensional TiO₂ nanostructured surface heterostructures: A review. Chem. Soc. Rev. 2014, 43, 6920–6937. [CrossRef]

126. Yang, G.; Chen, D.M.; Ding, H.; Feng, J.J.; Zhang, J.Z.; Zhu, Y.F.; Hamid, S.; Bahnemann, D.W. Well-designed 3D ZnIn₂S₄ nanosheets/TiO₂ nanobelts as direct Z-scheme photocatalysts for CO₂ photoreduction into renewable hydrocarbon fuel with high efficiency. Appl. Catal. B Environ. 2017, 219, 611–618. [CrossRef]

127. Di, T.M.; Zhu, B.C.; Cheng, B.; Yu, J.G.; Xu, J.S. A direct Z-scheme g-C₃N₄/SnS₂ photocatalyst with superior visible-light CO₂ reduction performance. J. Catal. 2017, 352, 532–541. [CrossRef]

128. Xia, Y.; Tian, Z.H.; Heil, T.; Meng, A.Y.; Cheng, B.; Cao, S.W.; Yu, J.G.; Antonietti, M. Highly Selective CO₂ Capture and Its Direct Photochemical Conversion on Ordered 2D/1D Heterojunctions. Joule 2019, 3, 2792–2805. [CrossRef]

129. Li, X.; Yu, J.G.; Jaroniec, M.; Chen, X.B. Cocatalysts for Selective Photoreduction of CO₂ into Solar Fuels. Chem. Rev. 2019, 119, 3962–4127. [CrossRef]

130. Anenberg, S.C.; Miller, J.; Minjares, R.; Du, L.; Henze, D.K.; Lacey, F.; Malley, C.S.; Emberson, L.; Franco, V.; Klimont, Z.; et al. Impacts and mitigation of excess diesel-related NOx emissions in 11 major vehicle markets. Nature 2017, 545, 467–471. [CrossRef]

131. Fang, R.M.; Huang, H.B.; Ji, J.; He, M.; Feng, Q.Y.; Zhan, Y.J.; Leung, D.Y.C. Efficient MnOₓ supported on coconut shell activated carbon for catalytic oxidation of indoor formaldehyde at room temperature. Chem. Eng. J. 2018, 334, 2050–2057. [CrossRef]

132. Stohl, A.; Aamaas, B.; Amann, M.; Baker, L.H.; Bellouin, N.; Berntsen, T.K.; Boucher, O.; Cherian, R.; Collins, W.; Daskalakis, N.; et al. Evaluating the climate and air quality impacts of short-lived pollutants. Atmos. Chem. Phys. 2015, 15, 10529–10566. [CrossRef]
133. Peng, M.Q.; Zhao, R.; Xia, M.; Li, C.J.; Gong, X.L.; Wang, D.; Xia, D.S. Study on the mechanism of NO removal by plasma-adsorption catalytic process. *Fuel* 2017, **200**, 290–298. [CrossRef]

134. Hermawan, A.A.; Chang, J.W.; Pasbakhsh, P.; Hart, F.; Talei, A. Halloysite nanotubes as a fine grained material for heavy metal ions removal in tropical biofiltration systems. *Appl. Clay Sci.* 2018, **160**, 106–115. [CrossRef]

135. Wang, T.; Liu, H.Z.; Zhang, X.Y.; Guo, Y.H.; Zhang, Y.S.; Wang, Y.; Sun, B.M. A plasma-assisted catalytic system for NO removal over CuCe/ZSM-5 catalysts at ambient temperature. *Fuel Process. Technol.* 2017, **158**, 199–205. [CrossRef]

136. Zhu, G.Q.; Li, S.P.; Gao, J.Z.; Zhang, F.C.; Liu, C.L.; Wang, Q.Z.; Hojamberdiev, M. Constructing a 2D/2D Bi$_2$O$_3$CO$_3$/Bi$_4$O$_5$Br$_2$ heterostructure as a direct Z-scheme photocatalyst with enhanced photocatalytic activity for NOx removal. *Appl. Surf. Sci.* 2019, **493**, 913–925. [CrossRef]

137. Shin, S.H.; Jo, W.K. Longitudinal variations in indoor VOC concentrations after moving into new apartments and indoor source characterization. *Environ. Sci. Pollut. Res.* 2012, **20**, 3696–3707. [CrossRef]

138. Sun, R.Z.; Shi, Q.M.; Zhang, M.; Xie, L.H.; Chen, J.S.; Yang, X.M.; Chen, M.X.; Zhao, W.R. Enhanced photocatalytic oxidation of toluene with a coral-like direct Z-scheme BiVO$_4$/g-C$_3$N$_4$ photocatalyst. *J. Alloy Compd.* 2017, **714**, 619–626. [CrossRef]

139. Wang, H.; Zhang, B.H.; Zhao, F.Q.; Zeng, B.Z. One-Pot Synthesis of N-GQDs Functionalized I-BiOCl Z-Scheme Cathodic Materials for “Signal-Off” Photoelectrochemical Sensing of Chlorpyrifos. *ACS Appl. Mater. Interfaces* 2018, **10**, 35281–35288. [CrossRef]

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