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Review (Special Issue on Photocatalysis in China)

A review on TiO₂-based Z-scheme photocatalystsKezhen Qi ^{a,b}, Bei Cheng ^a, Jiaguo Yu ^{a,d,*}, Wingkei Ho ^{c,#}^a State Key Laboratory of Advanced Technology for Materials Synthesis and Processing, Wuhan University of Technology, Wuhan 430070, Hubei, China^b Institute of Catalysis for Energy and Environment, College of Chemistry and Chemical Engineering, Shenyang Normal University, Shenyang 110034, Liaoning, China^c Department of Science and Environmental Studies, the Education University of Hong Kong, Tai Po, N. T. Hong Kong, China^d Department of Physics, Faculty of Science, King Abdulaziz University, Jeddah 21589, Saudi Arabia

ARTICLE INFO

Article history:

Received 18 October 2017

Accepted 31 October 2017

Published 5 December 2017

Keywords:

TiO₂

Z-scheme photocatalyst

Water splitting

CO₂ reduction

Pollutant degradation

ABSTRACT

TiO₂-based Z-scheme photocatalysts have attracted considerable attention because of the low recombination rate of their photogenerated electron–hole pairs and their high photocatalytic efficiency. In this review, the reaction mechanism of Z-scheme photocatalysts, recent research progress in the application of TiO₂-based Z-scheme photocatalysts, and improved methods for photocatalytic performance enhancement are explored. Their applications, including water splitting, CO₂ reduction, decomposition of volatile organic compounds, and degradation of organic pollutants, are also described. The main factors affecting the photocatalytic performance of TiO₂-based Z-scheme photocatalysts, such as pH, conductive medium, cocatalyst, architecture, and mass ratio, are discussed. Concluding remarks are presented, and some suggestions for the future development of TiO₂-based Z-scheme photocatalysts are highlighted.

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1. Introduction

The rapid development of various industries has led to an over-reliance on fossil fuel resources. This has exacerbated the global energy crisis and caused a range of environmental problems, thereby posing a serious threat to the long-term development of human society [1,2]. Therefore, it is essential to develop renewable energy sources that can replace fossil fuels. Much research effort has been devoted to finding a green and environment-friendly method to solve the problems associated with fossil fuels. Solar energy is clean, inexhaustible, and renewable. Thus, developing ways to efficiently utilize this energy source is of great importance [3]. Since Fujishima et al. [4] first

reported water splitting and hydrogen generation on TiO₂ photoelectrodes, studies on semiconductor photocatalysts have entered a new era [5–10]. Subsequently, the efficient stabilization of semiconductor photocatalysts has become an active area of research. Many semiconductors, such as TiO₂ [11–15], ZnO [16–19], SnO₂ [20–24], Fe₂O₃ [25], BiVO₄ [26–31], Cu₂O [32–36], and WO₃ [37–40], have been identified as potential photocatalysts under solar light. They have been used to catalyze a range of reactions, including water splitting for hydrogen generation [41,42], CO₂ reduction for hydrocarbon fuel production [43–49], decomposition of harmful gases [50,51], and degradation of organic pollutants [52–56]. Thus, they represent potential solutions to environmental pollution and the energy

* Corresponding author. Tel: +86-27-87871029; Fax: +86-27-87879468; E-mail: jiaguoyu@yahoo.com

Corresponding author. E-mail: keithho@eduhk.hk

This work was supported by the National Natural Science Foundation of China (51602207, 21433007, 51320105001, 21573170), the Self-determined and Innovative Research Funds of SKLWUT (2017-ZD-4, 2016-KF-17), and the Natural Science Foundation of Hubei Province of China (2015CFA001).

DOI: 10.1016/S1872-2067(17)62962-0 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 38, No. 12, December 2017

crisis.

TiO₂ has been extensively explored because of its ability to decompose organic pollutants combined with its corrosion resistance, nontoxicity, durability, and low cost [57]. However, the wide band gap of TiO₂ allows the absorption of only a small fraction of the solar spectrum (i.e., UV light), accounting for just ~4% of solar energy, which severely limits the application of this material [58]. Numerous methods, including metal/nonmetal doping [59–66], metal loading [67–77], heterojunction construction [78–85], and coupling with carbon materials [86–95], have been proposed to improve the photoconversion efficiency of TiO₂ photocatalysts. Enhancing the efficiency of photocatalysts requires a balance between the thermodynamics and kinetics of these reactions. Therefore, to improve the photocatalytic performance of TiO₂, two aspects should be considered: (a) reducing the band gap to broaden the spectral response range of light and (b) shifting the conduction band (CB) toward the negative and/or the valence band (VB) toward the positive, to thermodynamically benefit the photocatalytic redox reaction. However, these two goals are conflicting and are thus difficult to realize simultaneously in a single-component photocatalyst. Despite the extensive efforts devoted to TiO₂-based photocatalysts, their activity remains low [96,97]. The construction of heterostructures, which usually refers to type-I or type-II heterojunctions (Fig. 1), is widely considered a good method to enhance the photocatalytic activity [98]. However, the resulting redox sites, or photoexcited sites that release electrons and holes, are less active than in a single-component photocatalyst, resulting in a low redox capacity [99]. Therefore, new concepts are needed to devise heterostructured photocatalytic systems with greater reaction efficiency.

Z-scheme photocatalytic systems can satisfy both the above-mentioned requirements, namely, reducing the band gap of the semiconductors, while making the CB potential more negative and the VB potential more positive [100–103]. This system is a promising strategy for the improvement of photocatalysts [104–112]. As will be described, Z-scheme photocatalysts are named as such because their charge transfer mechanism is similar to natural photosynthesis in green plants, in which the charge-carrier transport pathway involves a two-step photoexcitation that resembles the English letter “Z” (Figs. 2 and 3) [113]. Unlike the traditional type-II heterojunction photocatalysts, the reactions in Z-scheme systems are driven by the photogenerated electrons (in the CB of PS I, see Section 2.1 below), which can maintain a high reducing ability,

Fig. 1. Schematic of the charge-carrier separation and transfer in conventional heterojunction photocatalysts. (A) type I; (B) type II.

Fig. 2. Mechanism of natural photosynthesis. Charge separation and transformation processes, including type-I and II reaction centers (similar to the Z-scheme). P680: pigment (chlorophyll) that can absorb 680 nm light in photosystem II (PS II); P680*: the excited state of P680; P700: pigment (chlorophyll) that can absorb 700 nm light in photosystem I (PS I); P700*: the excited state of P700. Mn: manganese–calcium complex; Tyr: tyrosine in PS II; Pheo: pheophytin, the primary electron acceptor of PS II; QA: plastoquinone electron acceptor; QB: secondary plastoquinone electron acceptor; PQ: plastoquinone; FeS: Rieske iron–sulfur protein; Cyt. f: cytochrome f; PC: plastocyanin; A0: phyloquinone; Fx, Fy, Fz: primary electron acceptors of PS I; A0, A1: two separate iron–sulfur centers; FD: ferredoxin; FNR: nicotinamide adenine dinucleotide phosphate (NADP) reductase [113].

Fig. 3. Schematic of electron transfer in a liquid-phase Z-scheme photocatalytic system (first generation Z-scheme photocatalytic system). The acceptor–donor pairs at each side compete for electrons to mediate the target reactions [116].

and the photogenerated holes (in the VB of PS II), which can sustain a high oxidizing ability. The charge-carrier transfer performed by Z-scheme photocatalysts is simple from a physics point of view. With their unique characteristics, Z-scheme photocatalysts are promising in various applications and have therefore been studied intensively.

This work reviews recent advances in the mechanistic understanding, application, and systematic improvement of TiO₂-based Z-scheme photocatalysts. Firstly, the development and basic principles of Z-scheme photocatalysts are described. Secondly, the improvement of TiO₂-based Z-scheme photocatalysts for photocatalytic applications, including water splitting, CO₂ reduction, decomposition of volatile organic compounds, and degradation of organic pollutants, is summarized. Thirdly, several methods for enhancing the performance of these photocatalysts in terms of various parameters, such as pH, conductive medium, cocatalyst, architecture, and mass ratio, are discussed. Finally, challenges and perspectives in future research on these photocatalysts are presented.

2. Mechanism of the Z-scheme photocatalytic reaction system

2.1. Natural photosynthesis

In nature, the Z-scheme photoinduced reaction system is an important component of the photosynthetic phase of green plants. This system consists of two photochemical reactions and a series of intermediate enzymes that promote redox reactions. The excitation and transfer processes of electrons are shown in Fig. 2 [113]. The two photochemical reactions take place in two corresponding systems, namely, photoreaction system I (photosystem I, denoted PS I) and photoreaction system II (photosystem II, denoted PS II). First, chlorophyll P680 (associated with PS II) is converted into the excited state P680* under solar light irradiation. At the same time, water molecules undergo oxidation, generating O₂ on chlorophyll P680. Under the action of cytochrome, protease, and other components, electrons are transferred from P680* to chlorophyll P700 (associated with PS I). Under solar light irradiation, chlorophyll P700 is excited to P700*. Under the action of the enzyme, the photogenerated electrons react with NADP⁺ to generate the reduced coenzyme II (nicotinamide adenine dinucleotide phosphate, NADP), which is used to reduce CO₂ and synthesize hydrocarbons [113,114]. A diagram of this electron transfer process forms a shape similar to the English letter “Z”, hence the name Z scheme. In natural photosynthesis, that is, Z-scheme photosynthesis, the production of oxygen and formation of NADP occur at two different parts. The two photosystems, PS I and PS II, harvest solar energy through an assembly of chlorophylls, and transfer electrons to a reaction center. Water oxidation occurs at a manganese–calcium oxide cluster on the donor side of PS II. At the acceptor side of PS I, CO₂ is reduced with the aid of NADP. The charge separation quantum efficiency is almost ideal, that is, close to 100%, under optimal conditions. Artificial Z-scheme photocatalysts are designed to imitate these characteristics of photosynthesis, by constructing a similar PS I and PS II reaction system that suppresses the recombination of electrons and holes.

2.2. Liquid-phase Z-scheme photocatalytic system

To mimic natural photosynthesis, the different materials of the optical systems PS I and PS II and the mediator (electron mediator, i.e., redox medium) must be chosen carefully to construct an artificial photosynthesis system, that is, traditional liquid-phase Z-scheme photocatalytic system (Fig. 3) [115,116]. The system shown in Fig. 3 does not involve direct contact between PS I and PS II, but rather, the reaction relies on the charge transport facilitated by redox electron mediators. Common redox mediators include Fe³⁺/Fe²⁺, IO₃[−]/I[−], [Co(bpy)₃]^{3+/2+}, NO₃[−]/NO₂[−], and [Co(phen)₃]^{3+/2+} [117–121]. Bard et al. [122] reported the use of a Z-scheme for water splitting in 1979. Upon exposure to sunlight, the electrons in the VB of PS II are excited by the absorption of photons and jump to the CB. Holes remain in the VB of PS II, oxidizing H₂O to O₂ while producing H⁺ ions. The excited electrons in the CB of PS II are consumed by reaction with the high-valence ion in the redox electron mediator. Meanwhile, the VB of PS I is excited by light too, and the electrons transfer to the CB to reduce H⁺ ions

to H₂. The holes in the VB of PS I react with the low-valence ions in the redox electron mediator to regenerate high-valence ions.

The electron acceptor (A) and donor (D) can also react with the photogenerated electrons in the CB of PS I and the holes in the VB of PS II, respectively. This reaction is thermodynamically more favorable than water splitting and will decrease the effective number of photogenerated electrons and holes available to conduct the target reactions. Therefore, backward reactions must be suppressed. Despite the extensive progress made in the development of artificial Z-scheme systems, they remain afflicted by various negative effects that need to be addressed. Firstly, the aforementioned backward reactions lead to a sharp decrease in the effective number of charge carriers and interfere with the water splitting reaction. Secondly, the redox mediators can, to various extents, absorb light at the same wavelengths as the photocatalysts, which reduces the amount of light absorption by the latter. Thirdly, the long-term stability and activity of the A/D redox mediators are currently insufficient. Lastly, for PS–A/D–PS systems, only liquid-phase photocatalytic reactions have been successfully developed thus far. However, various solid-state interfaces are currently being developed.

2.2. All-solid-state Z-scheme photocatalytic system

The structure of the all-solid-state Z-scheme system comprises a conductive solid medium connecting PS II and PS I (Fig. 4). Thus, the liquid A/D pair is no longer needed, and the aforementioned backward reactions are completely avoided, as described by Tada et al. [123] in 2006. Noble metal particles (such as Au and Ag) can be employed as electron mediators for the all-solid-state Z-scheme system to achieve high efficiency of charge-carrier separation and transport via the formation of an interface between PS II and PS I [123–126]. A conductor can also be inserted between PS II and PS I to form an ohmic contact with low contact resistance [127,128]. Thus, the photogenerated electrons in the CB of PS I and holes in the VB of PS II can be almost exclusively reserved for the desired reduction and oxidation reactions, respectively. Moreover, the absence of the A/D pair completely eliminates the shielding effect. As no A/D pair is necessary, PS–conductor–PS systems can work not only in the liquid phase but also the gas phase. Under light irradiation, the VBs of PS I and PS II retain their photogenerated holes when the electrons are excited to the corresponding CBs. Thus, the photogenerated holes in the VB of PS II show sufficiently strong oxidation ability to oxidize water and organic pollutants. The electrons in the CB of PS II and the holes in the VB of PS I

Fig. 4. Schematic of electron transfer in all-solid-state Z-scheme photocatalysts (second generation Z-scheme photocatalytic systems) [116].

are finally annihilated via the conductive medium. The excited electrons in the CB of PS I exhibit a strong reducing ability, which can be used for photocatalytic water splitting, hydrogen production, and CO₂ reduction.

2.3. Direct Z-scheme photocatalytic system

In 2013, Yu et al. [129] first proposed the concept of a direct Z-scheme photocatalyst to explain the mechanism of photocatalytic formaldehyde (HCHO) degradation in TiO₂/g-C₃N₄ composites. The direct Z-scheme system does not require a redox medium, and the charge carriers directly transfer across the interface of PS I and PS II. In this manner, the transmission distance is shortened, and the photocatalytic efficiency is improved. This reaction consists of two light-driven reaction systems, namely, I and II. Direct Z-scheme photocatalysts are structurally similar to the type-II heterojunction photocatalysts (Fig. 1(B)), but their charge-carrier transport mechanisms are different. In a typical type-II heterojunction photocatalyst, the CB and VB levels of PS II are higher than those of PS I. Under light irradiation, the photogenerated electrons in PS II and holes in PS I will transfer to the CB of PS I and VB of PS II, respectively, thereby achieving the spatial separation of the photogenerated electron-hole pairs. However, as the photogenerated electrons and holes, respectively, accumulate in the CB of PS I and VB of PS II, with a low reduction potential and low oxidation potential, the redox ability of this photocatalytic system will be greatly suppressed.

The direct Z-scheme system exhibits a different charge-carrier migration mechanism. Here, the photogenerated electrons in PS II, which have low reduction potential, will recombine with the photogenerated holes in PS I, which have low oxidation potential (Fig. 5). Therefore, the photogenerated electrons with high reduction potential, which are located in PS I, and the holes with high oxidation potential, located in PS II, can remain in their respective locations to achieve the spatial separation of charge carriers and optimize the redox ability of the photocatalytic system. The charge-carrier migration in the direct Z-scheme photocatalyst is physically more favorable than that in the type-II heterojunction. This is because the migration of electrons from the CB of PS II to the hole-rich VB of PS I is thermodynamically favored by the electrostatic attraction between the electrons and holes. Consequently, the direct Z-scheme system achieves superior photocatalytic perfor-

Fig. 5. Charge-carrier separation mechanism in the direct Z-scheme photocatalyst built from two different semiconductors (third generation Z-scheme photocatalytic system).

mance. Note that the charge-carrier separation mechanism of the direct Z-scheme photocatalyst is similar to that of the liquid-phase and all-solid-state Z-scheme photocatalysts, except that no redox medium is needed. Thus, the photogenerated charge carriers can directly migrate through the PS I–PS II interfaces and accelerate the charge-carrier separation efficiency of the photocatalytic system. Moreover, the absence of an expensive redox mediator greatly reduces the fabrication cost of the direct Z-scheme system. Clearly, then, this system offers three unique advantages, namely, rapid electron–hole separation efficiency, good redox ability, and low fabrication cost. With these advantages, this system shows immense potential in photocatalytic applications.

Both the direct and all-solid-state Z-scheme systems have certain requirements for the band structures of PS I and PS II. The potential of the CB of PS II must be lower than that of the VB of PS I. The more positive the VB potential of PS II is, the stronger the oxidation ability of the Z-scheme system will be. The more negative the CB potential of PS I is, the stronger the reduction ability of the Z-scheme photocatalytic system will be. As our understanding of Z-scheme systems develops, the liquid-phase Z-scheme system is expected to be gradually replaced with the direct and all-solid-state Z-scheme systems, because of the following disadvantages of the liquid-phase system. (a) Side reactions easily occur. The CB electrons of PS I can easily react with the high-valence ions in the redox electron mediator, and are thus wasted. Similarly, the holes are wasted by an analogous reaction in which they oxidize the low-valence ions in the redox mediator. (b) The light absorption by the semiconductor is blocked by the redox electron mediator, which absorbs part of the incident light. (c) The application range is narrow and is mostly limited to water splitting. The progress of research has yielded the development of direct Z-scheme photocatalysts without a redox mediator. The direct Z-scheme system can effectively overcome most of the problems of the traditional liquid-phase system. In the direct Z-scheme system, charge is transferred directly across the contact interface, the transformation distance is shortened, the occurrence of adverse reactions is reduced, and both the utilization rate of visible light and the photocatalytic efficiency are improved. As a result of the greater light utilization, this system is no longer limited to water splitting but can also be employed in other reactions, e.g., in the gas phase. In the TiO₂-based Z-scheme system, TiO₂ is usually used for the PS II component because of its relatively low VB position. The charge transfer mechanism of the TiO₂-based Z-scheme system is similar to those in the direct and all-solid-state Z-scheme systems. In the next section, some examples are presented to introduce the charge transfer mechanism in more detail.

3. Applications of TiO₂-based Z-scheme photocatalysts

TiO₂-based Z-scheme photocatalysts achieve excellent performance in a wide range of applications, such as water splitting, CO₂ reduction, decomposition of harmful gases, and degradation of organic pollutants. In this section, various photocatalytic applications of TiO₂-based Z-scheme photocatalysts

are summarized.

3.1. Water splitting

Hydrogen is a clean energy source, which generates water as its sole combustion product. Hydrogen has a high energy density and is expected to replace fossil fuels in the future. Photocatalytic water splitting is an ideal method for H₂ generation [130] that requires only a photocatalyst, solar light, and water [131,132]. In the past decade, many semiconductor-based photocatalysts have been used for this purpose, including SnO₂, C₃N₄, CdS, and TiO₂ [133–137]. However, the efficiency of H₂ production through photocatalytic water splitting is still extremely low and far from fulfilling the practical requirements of industry. This low efficiency is mainly caused by the low utilization of solar light and high electron–hole recombination rate in the photocatalysts [138–141]. In this context, Z-scheme photocatalysts can effectively suppress the electron–hole recombination by isolating the reduction and oxidation sites of the photocatalytic reaction. TiO₂-based Z-scheme photocatalysts have shown excellent performance in photocatalytic water splitting, and have been studied extensively for their potential to enhance the performance of current methods for H₂ production [142,143].

Recently, Xu et al. [144] successfully constructed a direct Z-scheme anatase/rutile bi-phase system for photocatalytic water splitting. This photocatalyst is synthesized by the electrospinning method and calcination (Fig. 6(A) and (B)), and the ratio of anatase and rutile can be controlled by tuning the cooling time. The thermodynamic stability of rutile is better than that of anatase. Therefore, fast cooling effectively inhibits the transformation of rutile into anatase and thus preserves the thermodynamic stability of the as-prepared nanofibers. The photocatalytic activity of H₂ production via water splitting is higher over the rapidly-cooled anatase/rutile nanofibers than over the pure anatase and pure rutile produced by slow cooling

(Fig. 6(C)). This is because the as-prepared TiO₂ nanofibers act as a direct Z-scheme anatase/rutile photocatalyst, which greatly reduces the electron–hole recombination rate. In addition, the electron–hole separation efficiency and redox ability of the sample prepared by the former process are better than those of the TiO₂ nanofiber prepared by slow cooling, because of the high reduction and oxidation potentials of Z-scheme photocatalysts. Moreover, an effective means to improve the photocatalytic performance is to deposit metal particles onto the surface of TiO₂. When Pt nanoparticles are photodeposited on TiO₂, they are preferentially deposited on the surface of rutile instead of anatase (Fig. 6(B)). This suggests that the photogenerated electrons tend to migrate to the CB of rutile because of the formation of the direct Z-scheme anatase/rutile system. The photocatalytic mechanism of the direct Z-scheme anatase/rutile system is shown in Fig. 6(D).

3.2. CO₂ reduction

Using photocatalytic technology to chemically reduce CO₂ into hydrocarbons not only transforms this greenhouse gas into reusable fuel but also helps alleviate global warming. However, CO₂ is an extremely stable compound, and reacting it directly is relatively difficult. Nevertheless, many methods have been developed for CO₂ reduction, including biological conversion, electrocatalysis, photocatalysis, and thermal catalysis. The solar photocatalytic conversion of CO₂ to hydrocarbon fuels in the presence of H₂O has received particular attention because it promises to alleviate society's current dependence on fossil fuels while lowering the CO₂ concentration in the atmosphere and thus decreasing the greenhouse effect. Nevertheless, photocatalytic CO₂ reduction as a solar-driven means of fuel production remains a challenge because of the low solar energy conversion efficiency, resulting from the low utilization efficiency of solar light and rapid electron–hole recombination rate of photocatalysts [43]. Fortunately, Z-scheme photocatalytic systems offer an effective option for highly efficient photocatalytic CO₂ reduction.

For example, Wei et al. [145] prepared all-solid-state Z-scheme photocatalysts for CO₂ reduction. These were based on Au@CdS/IO-TiO₂ prepared via the gas bubbling-assisted membrane reduction–precipitation (GBMR/P) method, in which Au@CdS consists of core(Au)–shell(CdS)-structured nanoparticles, and IO-TiO₂ has a well-defined three-dimensionally ordered macroporous (3DOM) inverse opal structure (Fig. 7(A)–(C)). The Au@CdS core-shell nanoparticles can be created with variable molar ratios of Cd/Au, and they are well dispersed and supported on the inner wall of 3DOM IO-TiO₂. The macroporous architecture of the catalyst denoted Au@CdS/IO-TiO₂-1 contains periodic voids with an average diameter of 195 ± 10 nm and wall thickness of 30 ± 5 nm (Fig. 7(C)). The thickness of the CdS shell over the Au core can be adjusted within 0–3 nm. The size of Au@CdS is in the range of 4–10 nm, with the mean diameter of the Au core being 3.5 ± 1.0 nm (Fig. 7(C)). Among the as-prepared catalysts, Au@CdS/IO-TiO₂-1 has a moderately thick CdS shell and offers the highest photocatalytic activity and selectivity for CO₂ re-

Fig. 6. TEM (A) and HRTEM (B) images of the mixed-phase composite of anatase and rutile TiO₂ with photodeposited Pt nanoparticles. (C) Comparison of photocatalytic H₂ production activities of A400, SC500, RC500, and R800 samples. (D) Schematic of the water splitting mechanism of the direct Z-scheme anatase/rutile photocatalyst [144].

Fig. 7. SEM (A), TEM (B), and HRTEM (C) images of Au@CdS/IO-TiO₂-1 Z-scheme photocatalyst; (D) Photocatalytic activity and stability of Au@CdS/IO-TiO₂-1 catalyst in terms of the formation rate of H₂, CH₄, and CO for five test cycles; (E) Schematic of the photocatalytic CO₂ reduction mechanism of the Z-scheme Au@CdS/IO-TiO₂ photocatalyst [145].

duction. When this catalyst is used in CO₂ reduction, the formation rate of CH₄ is 41.6 μmol g⁻¹ h⁻¹, and the selectivity to CH₄ production is 98.6%. Moreover, the Au@CdS/IO-TiO₂ catalysts show a stable structure and photocatalytic activity across multiple reaction cycles (Fig. 7(D)). Fig. 7(E) shows the photocatalytic mechanism underlining the Z-scheme system with the CdS(shell)-Au(core)-TiO₂(support) junction. As can be seen, this system promotes the separation of photogenerated electrons and holes via the sequential electron transfer of TiO₂→Au→CdS.

3.3. Decomposition of volatile organic compounds

As a side effect of the technological drive towards improved living standards, high concentrations of airborne pollutants are continuously released from various sources, such as building decoration processes, automobile exhaust emissions, and livestock farming. This high level of pollution is a frequent cause of various diseases. Many indoor building materials emit harmful volatile organic compounds (VOCs). HCHO is a typical indoor hazardous gas that can cause skin diseases, respiratory diseases, leukemia, and many others. TiO₂-based Z-scheme photocatalysts have been demonstrated to be effective in destroying VOCs [129,146]. Recently, increasing efforts have been devoted to improving the design and fabrication of these photocatalysts to enhance their performance.

For example, Yu et al. [129] reported the photocatalytic decomposition of the indoor VOC pollutant HCHO using a direct TiO₂/g-C₃N₄ Z-scheme photocatalyst. A series of such photocatalysts can be synthesized through simple calcination by

mixing and calcining P25, TiO₂, and different amounts of urea. During calcination, the urea in the mixture is polycondensed into g-C₃N₄ and is deposited onto the TiO₂ surface, as shown in the TEM image in Fig. 8(A). The size of the TiO₂ nanoparticles is approximately 30 nm, and they are uniformly covered by a thin sheet of g-C₃N₄. Intimate contact between TiO₂ and g-C₃N₄ is created, thereby enabling the rapid transport of charge carriers across the contact interface. In this synthetic method, the actual loading contents of g-C₃N₄ in the samples U20, U100, U200, and U500 are estimated to be 3, 12, 18, and 26 wt%, respectively. The samples were investigated for their performance in the photocatalytic decomposition of airborne HCHO at room temperature. The HCHO decomposition ability of TiO₂ increased as the content of g-C₃N₄ increased from 0 to 12 wt% (Fig. 8(B)).

The mechanism of this direct Z-scheme photocatalytic reaction has been elucidated by radical trapping experiments. The formation of hydroxyl radicals (•OH) on the irradiated sample surfaces is detected through the photoluminescence (PL) method, using terephthalic acid (TA) as a probe molecule. This method relies on detecting the PL signal at 425 nm arising from the TA-OH adduct. For the U0, U20, U100, U200, and U500 samples, the PL intensity gradually increases as the irradiation time is prolonged (Fig. 8(C)). This trend indicates the production of •OH radicals. Meanwhile, no irradiation-induced PL signal is observed from the pure g-C₃N₄ sample. If the coupling of g-C₃N₄ and TiO₂ resulted in a type-II heterojunction, instead of a direct Z-scheme heterojunction, no time-dependent increase in PL intensity should be observed, because the photogenerated holes would accumulate in the VB of g-C₃N₄, which does not have sufficient oxidation power to produce •OH radi-

Fig. 8. (A) High-resolution TEM images of optimized composition of $\text{TiO}_2/\text{g-C}_3\text{N}_4$ (U100). (B) Comparison of photocatalytic formaldehyde degradation performances of U0, U20, U100, U200, U500, and $\text{g-C}_3\text{N}_4$. (C) PL spectral changes observed during UV irradiation of the samples in 2×10^{-3} mol/L NaOH solution in the presence of 5×10^{-4} mol/L terephthalic acid. Comparison of PL intensity at 425 nm against UV irradiation time for pure P25, U20, U100, U200, U500, and pure $\text{g-C}_3\text{N}_4$ samples. (D) Scheme illustrating band positions of $\text{g-C}_3\text{N}_4$ and TiO_2 together with $\text{OH}^-/\bullet\text{OH}$ and O_2/O_2^- redox potentials. (E) Illustration of (hypothetical) conventional $\text{TiO}_2/\text{g-C}_3\text{N}_4$ type-II heterojunctions, which do not form. (F) Schematic of the charge transfer and separation in direct $\text{TiO}_2/\text{g-C}_3\text{N}_4$ Z-scheme photocatalysts under UV light irradiation [129].

icals (Fig. 8(C) and (D)). The observed production of $\bullet\text{OH}$ radicals confirms the accumulation of photogenerated holes in the VB of TiO_2 rather than $\text{g-C}_3\text{N}_4$. Thus, it is clear that a direct Z-scheme system is formed in the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ heterojunction (Fig. 8(E) and (F)). Moreover, the photocatalytic activity of the direct $\text{TiO}_2/\text{g-C}_3\text{N}_4$ Z-scheme photocatalysts is greatly influenced by the amount of $\text{g-C}_3\text{N}_4$ loaded on TiO_2 . Excessive content of $\text{g-C}_3\text{N}_4$ on TiO_2 causes a decrease in photocatalytic activity (Fig. 8(B)). This occurs because the overloading of $\text{g-C}_3\text{N}_4$ effectively shields the TiO_2 and inhibits the contact between TiO_2 and the reactant. This finding suggests that careful tuning of the chemical composition of the semiconductors in a direct Z-scheme photocatalyst is crucial for enhanced photocatalytic performance.

The mechanism of direct Z-scheme photocatalysis in the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ system was further studied by Liu et al. [147] on the basis of density functional theory calculations. The three-dimensional charge density difference at the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ interface was calculated to obtain a clear picture of the charge-carrier migration (Fig. 9). The interface between $\text{g-C}_3\text{N}_4$ and TiO_2 is the center of the charge-carrier redistribution (Fig. 9(A)). The formation energy of the interface was calculated to be -1.16 eV. This negative energy indicates that the interface is stable, therefore allowing efficient charge-carrier migration between TiO_2 and $\text{g-C}_3\text{N}_4$. At the same time, a negligible change in charge density is observed in the interior of TiO_2 , where only a small amount of interfacial contact between $\text{g-C}_3\text{N}_4$ and TiO_2 occurs. In Fig. 9(B), the planar-averaged charge density difference along the Z direction is given. As can be seen, charge redistribution mostly occurs around the interface. The electrons flow directly from $\text{g-C}_3\text{N}_4$ to TiO_2 , whereas the holes stay in $\text{g-C}_3\text{N}_4$. In other words, an induced electric field across the in-

terface follows the direction from $\text{g-C}_3\text{N}_4$ to TiO_2 because of the net charge accumulation. The charge-carrier diffusion between TiO_2 and $\text{g-C}_3\text{N}_4$ continues until charge equilibrium is obtained. As a result, the net charge-carrier accumulation causes the formation of an internal electric field at the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ interface. As shown in Fig. 9(C), this electric field facilitates injection of the electrons from TiO_2 to $\text{g-C}_3\text{N}_4$ upon irradiation. The formation of an internal electric field between $\text{g-C}_3\text{N}_4$ and TiO_2 has also been found to benefit the charge-carrier transfer efficiency of the direct Z-scheme. Upon light irradiation, the induced internal electric field accelerates the charge-carrier separation across the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ interface, which is central to the direct Z-scheme mechanism.

3.4. Degradation of organic pollutants

Industrial development has exacerbated environmental pollution and released large amounts of organic contaminants, resulting in serious ecological damage [22,148,149]. Large amounts of toxic organic pollutants, both airborne and ground-based, are also transported into wastewater streams. Water pollution by organic pollutants causes serious environmental problems and poses a severe threat to human health. Various chemical and physical methods have been applied to treat these contaminants. Semiconductor photocatalysts have captured considerable attention because of their ability to utilize solar energy, a sustainable source, for the degradation of organic pollutants without causing environmental side effects [150]. Although various semiconductor photocatalysts have been studied for this application, their photocatalytic performance still does not satisfy real-life requirements. Therefore, attention has switched to the development of novel photocata-

Fig. 9. (A, B) Charge density difference ($\Delta\rho$) and planar-averaged view of $\Delta\rho$ of $\text{TiO}_2/\text{g-C}_3\text{N}_4$. The yellow and cyan areas respectively indicate electron accumulation and depletion. (C) The proposed Z-scheme photocatalytic mechanism for the $\text{TiO}_2/\text{g-C}_3\text{N}_4$ system [147].

lytic systems with higher activities. Z-scheme photocatalysts show particular promise for photocatalytic pollutant degradation because of their efficient separation of photogenerated electron-hole pairs and ability to maximize the redox potential of the system.

Xie et al. [151] prepared a CdS-Ag-TiO_2 Z-scheme photocatalyst through the electrochemical method. First, anatase TiO_2 nanotubes (NTs) are synthesized via anodization of Ti foil (Fig. 10(A)). Then, Ag nanoparticles are deposited on the TiO_2 NTs by the pulsed current method. Finally, a CdS shell layer is cathodically electrodeposited on the surface of the as-prepared Ag nanoparticles. These Ag@CdS cores uniformly attach to the surface of the TiO_2 NTs (Fig. 10(B)), with Ag nanoparticles as the intermediary between CdS and TiO_2 . The CdS-Ag-TiO_2 NTs

show a higher photocurrent density than that of other NT-based materials because of the formation of a CdS-Ag-TiO_2 Z-scheme heterojunction, which greatly reduces electron-hole recombination (Fig. 10(C)). The photocatalytic activity of CdS-Ag-TiO_2 for the degradation of methylene blue (MB) is higher than that of pure TiO_2 NTs, Ag-TiO_2 NTs, and CdS-TiO_2 NTs (Fig. 10(D)).

4. Strategies to enhance the activity of Z-scheme TiO_2 -based photocatalysts

The activities of TiO_2 -based Z-scheme photocatalytic systems can be enhanced by controlling several parameters including pH value, electron mediator, impurity doping, cocata-

Fig. 10. Scanning electron microscopy top-view images of TiO_2 NTs (A) and CdS-Ag-TiO_2 NTs (B). The insets show the cross-sectional images of the corresponding samples on the same scale. Photocurrent response (C) and photocatalytic degradation (D) of methylene blue under UV light irradiation on pure TiO_2 NTs, Ag-TiO_2 NTs, CdS-TiO_2 NTs, and Ag-CdS-TiO_2 NTs [151].

lyst, architecture, and mass ratio. These factors are discussed in the following sections.

4.1. pH value

The activity of photocatalysts is greatly influenced by the pH of the reaction solution. Most photocatalytic reactions are carried out under neutral conditions, while some photocatalysts have shown high photocatalytic activity under acidic conditions [152], and others are favorable under alkaline conditions [115]. The effect of pH on the photocatalytic system can mostly be attributed to three mechanisms, as follows: (a) altering the band structure, including band positions and band gap [153], (b) altering the adsorption ability with regard to the target pollutants via changes in surface charge [154], and (c) altering the production rate of the active species in the photocatalytic system, e.g., $\bullet\text{OH}$ or $\bullet\text{O}_2^-$. Thus, pH control is vital in a Z-scheme photocatalyst [155,156].

For example, in the $\text{Pt}/\text{TiO}_2(\text{anatase})-\text{TiO}_2(\text{rutile})-\text{IO}_3^-/\text{I}^-$ Z-scheme system [115], the photocatalytic efficiency of water splitting increases with increasing pH until the value reaches 9. Then, the catalytic efficiency starts to decrease. The detailed mechanism can be described as follows: when $\text{pH} < 3$, I^- is oxidized to I_3^- at the surface of $\text{Pt}/\text{TiO}_2(\text{anatase})$, whereas H_2O cannot be oxidized to produce oxygen. Meanwhile, I_3^- mostly absorbs light at a short wavelength of 350 nm. Thus, the photocatalytic efficiency of the system is very low. When $3 < \text{pH} < 9$, the oxidation products of I^- are both I_3^- and IO_3^- . Therefore, the catalytic efficiency gradually increases with the increasing supply of IO_3^- . Under alkaline conditions, the sole oxidation product of I^- is IO_3^- . Thus, the $\text{Pt}/\text{TiO}_2(\text{anatase})-\text{TiO}_2(\text{rutile})-\text{IO}_3^-/\text{I}^-$ system performs more

favorably in alkaline conditions.

In a direct Z-scheme photocatalytic system, no electron mediator is involved. The sign of charge (positive or negative) on the solid surface heavily depends on the isoelectric point and pH of the solution. For example, in the Z-scheme $\text{BiVO}_4-\text{Ru}/\text{SrTiO}_3:\text{Rh}$ system, the highest photocatalytic activity for water splitting is achieved at $\text{pH} = 3.5$ (Fig. 11(A)) [152]. Optical microscope observation shows that among $\text{pH} = 7.0, 4.0, 3.5$, and 2.5 , $\text{pH} = 3.5$ supports the highest degree of powder aggregation of BiVO_4 and $\text{Ru}/\text{SrTiO}_3:\text{Rh}$, as these species respectively display negative and positive charges at this pH because of the match between the zeta potential of BiVO_4 and the isoelectric point of $\text{SrTiO}_3:\text{Rh}$. This phenomenon is responsible for the electrostatic attraction between the two species in powder form. Under neutral conditions, the powders are well dispersed (Fig. 11(B)). The solid–solid contact interface contributes to the high quantum yield of 1.7% at 420 nm and the high solar energy conversion efficiency of 0.12%.

Similarly, Miyauchi et al. [157] constructed a direct Z-scheme system of $\text{WO}_3/\text{CaFe}_2\text{O}_4$. The CaFe_2O_4 surface is negatively charged in aqueous solution at $\text{pH} = 7$. Thus, neutral conditions effectively promote the selective nucleation of WO_3 particles on the CaFe_2O_4 surface, resulting in a significant increase in the photocatalytic activity of the $\text{WO}_3/\text{CaFe}_2\text{O}_4$ composite for the decomposition of acetaldehyde under visible-light irradiation. However, at acidic pH, the as-prepared WO_3 particles remain in the solution as free particles, that is, they are not effectively attached on the CaFe_2O_4 surface, resulting in low activity. Therefore, pH adjustment should be included in the design of these direct Z-scheme systems.

4.2. Electron mediators

The rate at which the photogenerated charge carriers cross the interface between PS II and PS I is greatly influenced by the degree of closeness of the contact surfaces in Z-scheme photocatalysts. Solid conductors, which offer high electrical conductivity, good stability, and no adverse reaction, are an increasingly popular choice as the electron transmission medium. At the interface between the two semiconductors (PS II and PS I), the use of a low-ohmic solid contact not only facilitates the transfer of photoinduced electrons from the CB of PS II to the VB of PS I but also avoids the effect of liquid-phase reactions on the Z-scheme system.

To date, a range of highly conductive solids, such as Au, Ag, Pt, and other metals, and layered reduced graphene oxide (RGO), have been selected as the transmission medium for the Z-scheme systems. Z-scheme $\text{CdS}/\text{Au}/\text{TiO}_2$ nanojunction systems have been produced, and show higher photocatalytic activity than single and two-component systems for the decomposition of organic compounds [123,158]. In such systems, the photoinduced electrons undergo a sequential transfer: $\text{TiO}_2 \rightarrow \text{Au} \rightarrow \text{CdS}$ (Fig. 12). In addition, the effects of different noble metals (such as Au and Ag) on the photocatalytic activity of such systems have been studied. More recently, Shen et al. [159] have synthesized similar $\text{CdS}/\text{M}/\text{TiO}_2$ ($\text{M} = \text{Ag}, \text{Ru}, \text{Au}, \text{Pd}$, and Pt) systems using a two-step photodeposition method.

Fig. 11. (A) Dependence of the photocatalytic activity of the $(\text{Ru}/\text{SrTiO}_3:\text{Rh})-(\text{BiVO}_4)$ system on pH (adjusted with H_2SO_4 and NaOH). Catalyst: 0.1 g each; Light source: 300 W Xe-arc lamp with a cutoff filter ($\lambda > 420 \text{ nm}$). (B) Suspension of $\text{Ru}/\text{SrTiO}_3:\text{Rh}$ and BiVO_4 at neutral and acidic conditions [152].

Fig. 12. (A) Photodecomposition of MB catalyzed by CdS/M/TiO₂ (M = Ag, Ru, Au, Pd, and Pt) systems under visible-light irradiation (>400 nm). (B) Energy band diagram and charge transfer mechanism in CdS/M/TiO₂ systems [159].

Their photocatalytic activities for MB degradation in aqueous solution under visible-light irradiation are superior to that of the CdS/TiO₂ system. Moreover, the photocatalytic activity is significantly dependent on the type of noble metal used, as explained by the influence of charge transfer on the work function of these metals. In the work of Shen et al., CdS/Ag/TiO₂ showed the best photocatalytic performance (Fig. 12(A)). The charge transfer in CdS/M/TiO₂ systems is illustrated in Fig. 12(B). Notably, the Fermi energy level of the metal will affect the interfacial charge transfer and thus the charge separation in the CdS/M/TiO₂ system. The minimum energy required to move an electron from the Fermi energy level into vacuum is defined as the work function [160], which for the above metals follows the order Ag < Ru < Au < Pd < Pt (Fig. 12(B)). This trend correlates well with the photocatalytic activities of the CdS/M/TiO₂ systems.

Aside from the noble metals discussed above, some non-metal materials and metal oxides with high conductivities can also be used as electron mediators in Z-scheme systems. For example, RGO can be employed as a solid-state electron mediator to promote electron transfer [161–165]. Recently, Kudo et al. [166] have also used RGO to build Z-scheme systems with various metal sulfides. The system composed of CuGaS₂ and RGO–TiO₂ can continuously split water for 12 h, with a 1.3% apparent quantum yield under 380 nm monochromatic light irradiation. Additionally, Takayama et al. [167] reported a PS

II–RGO–PS I Z-scheme system with the composition CuGaS₂–RGO–TiO₂ for the liquid-phase reduction of CO₂ under UV–visible irradiation (Fig. 13). In this study, CuGaS₂ acted as a reduction center, whereas TiO₂ acted as an O₂ evolution center, and the mediator RGO facilitated the electron transfer from the CB of TiO₂ to the VB of CuGaS₂. Although the photocatalytic activities are negligible in the absence of RGO, in the presence of RGO the system not only exhibits the photocatalytic production of CO (0.15 μmol h⁻¹) but also simultaneously produces O₂ and large amounts of hydrogen (28.8 μmol h⁻¹). This photocatalytic activity enhancement is attributed to the fast filling of the photogenerated holes in PS I with the photogenerated electrons in PS II via the conductive electron mediator.

4.3. Cocatalyst

The choice of metal, such as Au, Pt, Ru, and RuO₂, plays a key role in the Z-scheme photocatalytic system [168–170]. The mediator between the surfaces of PS I and PS II performs two important functions: to serve as an electron sink to enhance the separation of photogenerated charge carriers in PS I, and to offer active sites for H₂ evolution which have a lower potential than on the PS I and PS II surfaces.

An alternative approach was demonstrated by Hu et al. [171], who fabricated carbon-coated TiO₂/WO₃ nanofibers by combining the electrospinning technique (for the synthesis of

Fig. 13. (A) Schematic of the Z-scheme charge transfer and CO₂ reduction and (B) photocatalytic evolution of H₂, O₂, and CO on CuGaS₂–RGO–TiO₂ under UV–visible-light irradiation [167].

the nanofibers) and the hydrothermal method (for coating the carbon shell). The H_2 generation rate of the carbon-coated TiO_2/WO_3 nanofibers is considerably faster than those of pure TiO_2 nanofibers, TiO_2/WO_3 nanofibers, and $TiO_2@carbon$ core-shell nanofibers. This enhanced performance of photocatalytic water splitting can be attributed to the formation of a new type of Z-scheme system of TiO_2/WO_3 . Here, the carbon shell on the surface of TiO_2 acts as an electron collector, and WO_3 as a hole collector, ensuring that the photogenerated carrier pairs from both oxides are effectively separated. Therefore, more of the photogenerated electrons in TiO_2 are available via the carbon shell to reduce H^+ to H_2 , resulting in highly efficient photocatalytic H_2 evolution.

Elsewhere, Jo et al. [172] synthesized another new type of Z-scheme catalyst: MoS_2 nanosheets (NSs) covered on Z-scheme $TiO_2/g-C_3N_4$ composites, prepared by the wetness impregnation method. The MoS_2 NS-loaded Z-scheme $TiO_2/g-C_3N_4$ nanocomposites exhibited higher photocatalytic activity for the degradation of organic waterborne pollutants compared with pure TiO_2 , C_3N_4 , and TiO_2/C_3N_4 . This enhanced activity was driven by the improved separation of electron-hole pairs (generated by the visible-light irradiation of C_3N_4) at the $TiO_2/g-C_3N_4$ interface. The enhanced activity of these composites can also be partly attributed to the MoS_2 layer, which functions as both an electron sink and electron relay.

Recently, Gao et al. [173] synthesized ternary Z-scheme $TiO_2/WO_3/Au$ heterostructure composite nanofibers by the electrospinning technique. In this system, the role played by the carbon shell in the above-mentioned nanofibers was instead played by the gold particles loaded on the surface of the

TiO_2/WO_3 nanofibers, and the charge-carrier transport was greatly improved by the presence of multiple channels. The H_2 production rate of the as-prepared Z-scheme $TiO_2/WO_3/Au$ composites was greatly enhanced compared with that of the pure TiO_2 nanofibers and TiO_2/WO_3 nanofibers. Fig. 14 illustrates the reaction mechanism. Under UV light irradiation, both oxides are excited; then, the photogenerated electrons transfer from the CB of WO_3 to the VB of TiO_2 , and recombine with the holes of TiO_2 , thereby promoting the transfer of the photogenerated electrons of TiO_2 from the CB of TiO_2 to the Au nanoparticles. In this system, Au is the electron collector and WO_3 is the hole collector, thus supporting charge separation. Under UV-visible irradiation, the hot plasmonic electrons of Au are transported to the CB of TiO_2 , improving the H_2 production rate. Therefore, the Au nanoparticles play two major roles in this $Au/TiO_2/WO_3$ heterojunction photocatalyst system. In fact, the enhanced activity can be attributed to three causes: the Schottky effect, the formation of a Z-scheme heterojunction system, and the surface plasmon resonance effect of Au.

4.4. Doping

The main problem limiting the practical application of TiO_2 is its wide band gap (3.0–3.2 eV), which requires UV light irradiation to produce the excited charge carrier pairs. Thus, extending the light absorption range of TiO_2 to the visible range is highly desired. The most widely used method for this purpose has been the doping of impurities in TiO_2 , ever since the first report by Asahi et al. [174] of the photoabsorption and photocatalytic activity of anionic nitrogen-doped TiO_2 under visi-

Fig. 14. Schematic of the photocatalytic H_2 generation over ternary $TiO_2/WO_3/Au$ composite nanofibers [173].

ble-light irradiation. Not only nitrogen, but various other metals/nonmetals can be doped, which introduces new energy levels between the HOMO and LUMO to effectively reduce the TiO_2 band gap [175,176]. Although the doping of metals into TiO_2 is an effective way to enhance its photocatalytic activity, such catalysts are still not widely employed because of their susceptibility to photocorrosion, which greatly reduces their long-term stability [177].

Recently, the use of nonmetal dopants, such as iodine, nitrogen, sulfur, and carbon, to replace the oxygen atoms in the TiO_2 lattice has been reported to increase the photostability over that of metal-doped catalysts. In nonmetal-doped TiO_2 , a new energy level is introduced above the VB of TiO_2 , thus reducing the band gap and increasing the range of light-responsiveness. If the system is designed such that the doped TiO_2 acts as PS I and another semiconductor as PS II, the role of reduction will be played by PS II and that of oxidation by PS I. For example, Kondo et al. [178] demonstrated such a system by impurity doping into the TiO_2 component of a direct Z-scheme TiO_2 heterojunction, thus enhancing the photocatalytic performance of TiO_2 . Specifically, a visible-light-responsive $\text{TiO}_2/\text{g-C}_3\text{N}_4$ direct Z-scheme photocatalyst for H_2 production was prepared through a simple one-pot solvothermal route with the assistance of concentrated nitric acid. Upon S doping,

the S-doped $\text{TiO}_2/\text{g-C}_3\text{N}_4$ exhibited a red-shifted light-absorption band edge compared with the non-doped composite (Fig. 15(A)), confirming that the incorporation of S atoms into TiO_2 extends the light-absorption range of the samples and enhances their visible-light reactivity. Meanwhile, the formation of a direct Z-scheme heterojunction between S-doped TiO_2 and $\text{g-C}_3\text{N}_4$ markedly improved their charge transfer and separation efficiency for the photocatalytic reaction. As a result, the S-doped $\text{TiO}_2/\text{g-C}_3\text{N}_4$ composite, denoted p-SC (prepared by planetary ball mill synthesis), demonstrated a much higher photocatalytic performance for acetaldehyde decomposition than that of S-doped TiO_2 and $\text{g-C}_3\text{N}_4$ alone (Fig. 15(B)). The action spectral analysis and PL measurements indicated that Z-scheme charge transfer occurs over p-SC under visible-light irradiation. p-SC possesses high oxidative ability, whereas $\text{g-C}_3\text{N}_4$ possesses high reductive ability (Fig. 15(C) and (D)). Therefore, doping is a simple method for extending the light-absorption range of the individual semiconductors in a direct Z-scheme photocatalyst to achieve activity under visible as well as UV light.

4.5. Architecture

The properties of photocatalytic materials are closely relat-

Fig. 15. (A) Diffuse reflectance spectra of (a) TiO_2 (no treatment), (b) S- TiO_2 (sulfur-doped TiO_2), (c) p-SC (S- TiO_2 , $\text{g-C}_3\text{N}_4$, treated by planetary ball mill), (d) a-SC (S- TiO_2 , $\text{g-C}_3\text{N}_4$, treated by agate mortar), (e) s-SC (S- TiO_2 , $\text{g-C}_3\text{N}_4$, treated by sonication), (f) p- $\text{g-C}_3\text{N}_4$ ($\text{g-C}_3\text{N}_4$, treated by planetary ball mill), and (g) $\text{g-C}_3\text{N}_4$ (no treatment). (B) Time courses of CO_2 evolution from acetaldehyde decomposition over (a) p-SC, (b) a-SC, (c) s-SC, (d) S- TiO_2 , and (e) $\text{g-C}_3\text{N}_4$ under visible-light irradiation. (C) Action spectra for the decomposition of acetaldehyde using (a) p-S- TiO_2 , (b) p-TC, (c) p-SC, and (d) p- $\text{g-C}_3\text{N}_4$. (D) Schematic images of photocatalytic reaction and PL emission of (a) p-TC and (b) p-SC under visible-light irradiation [178].

ed to their architectures. The photocatalytic performance of the same material will vary greatly as a function of changes in its microarchitecture. These changes lead to different photocatalytic reaction mechanisms, exerting a great influence on the catalytic activity [179–182]. The influence of microarchitecture on photocatalytic performance is attributed mostly to three factors: (a) the light harvesting performance; (b) the stability and agglomeration tendency of the photocatalyst; and (c) the interfacial properties. Note that improvements to the light harvesting performance can be achieved in two ways: increasing the specific surface area of the photocatalyst; and controlling the morphology of the photocatalyst to increase the reflection and scattering of incident light among its constituent nanoparticles.

For example, Wei et al. [183] synthesized Pt@CdS nanoparticles, which adopt a 3DOM TiO₂-supported core-shell architecture, via the GBMR/P method. This catalyst possesses interconnected networks of spherical voids, and the Pt@CdS core-shell nanoparticles, which can have variable molar ratios of Cd/Pt, are well dispersed and attach to the inner walls of the voids. The 3DOM architecture benefits light harvesting by prolonging the light path length via enhancing the random light scattering in the interior. Moreover, this CdS(shell)–Pt(core)–TiO₂(support) nanojunction favors the separation of photogenerated charge carriers by promoting the

sequential electron transfer of TiO₂→Pt→CdS. Therefore, 3DOM Pt@CdS/TiO₂ catalysts possess superior photocatalytic performance for reduction of CO₂ to CH₄. To improve the stability of photocatalysts and to prevent their agglomeration, synthesizing them in the form of nanoarrays is a common method [151,184]. For example, Xian et al. [180] synthesized a TiO₂ NT array–graphene–CdS quantum dot composite film, showing enhanced photoactivity and photostability for the degradation of Rhodamine B (RhB).

Elsewhere, Ding et al. [185] inspired by natural Z-scheme photosynthesis and the anti-reflection morphology of the wings of black butterflies, have employed the wings of *Papilio nephele* as the templates to synthesize CdS/Au/TiO₂ architectures with improved light utilization. The Au cores and CdS shells were loaded on the membrane-architecture TiO₂ by similar two-step photodeposition methods, forming the Z-scheme TiO₂–Au–CdS system (Fig. 16(A)–(D)). This combination successfully enhanced the light harvesting and water splitting efficiency [185]. Following the same design principles, a wing-architecture TiO₂ (WATO) has also been prepared by an immersion–calcination method [185]. However, the WATO obtained in that case was a mixture of scale-architecture TiO₂ (SATO) and membrane-architecture TiO₂ (MATO). According to finite-difference time-domain simulations, the SATO component in the WATO system has lesser light reflection and trans-

Fig. 16. Morphology of Au/WA-TiO₂ and CdS/Au/WA-TiO₂ and their photocatalytic activities for water splitting for hydrogen generation: (A) FESEM images of Au/WA-TiO₂; (B) TEM images of Au/WA-TiO₂; (C) TEM images of CdS/Au/WA-TiO₂; (D) HRTEM image showing CdS/Au with a core-shell structure formed on WA-TiO₂ substrate; (E) UV-visible absorption spectra of PA-TiO₂, WA-TiO₂, SA-TiO₂, CdS/Au/WA-TiO₂, and CdS/Au/PA-TiO₂; (F) H₂ generation of the samples (50 mg) under UV and visible-light irradiation [185].

mission than MATO. Besides, the absorbance of SATO is higher in water than in air because of the difference in the refraction indices (Fig. 16(E)). However, this medium-dependent absorbance is not seen in MATO. This behavior is attributed to the multiple scattering and diffuse reflection of light in the quasi-honeycomb architecture of SATO, resulting in prolonged light-transfer path lengths. Moreover, SATO is presumed to be the main light-harvesting center in the photocatalytic reaction, whereas MATO serves as an assistant during light harvesting. The H_2 production rate of WATO–Au–CdS is approximately 133% higher than that of MATO–Au–CdS (Fig. 16(F)). Thus, the design of macroscopic architecture is crucial for the construction of Z-scheme photocatalytic systems.

Naturally, the interface formed between the crystal facets of PS I and PS II also affects the activity of Z-scheme photocatalysts [176]. Specifically, the crystal indices of the interfacial facets can greatly influence the pollutant degradation performance of such photocatalysts. For example, Huang et al. [186] synthesized $g\text{-C}_3\text{N}_4/\text{TiO}_2$ Z-scheme photocatalysts by a simple microwave-assisted method, wherein TiO_2 consisted of a hollow nanobox (HNB) assembled from TiO_2 NSs. They then investigated the dependence of the photocatalytic performance on the facets of TiO_2 that were used to form the interface. The TiO_2 NSs contact with the $g\text{-C}_3\text{N}_4$ mainly through the (001) facets (Fig. 17(A)), whereas the TiO_2 HNBs mainly contact through the (101) facets (Fig. 17(B) and (C)). Under light irradiation, the photogenerated electrons and holes of the TiO_2 accumulate at the (101) and (001) facets, respectively (Fig. 17(D)), because of the surface heterojunction formed between those two facets [187]. Then, as shown in Fig. 17(B) and (C), the photogenerated electrons that accumulate at the (101) facets of the TiO_2 nano-

particles can easily migrate to the VB of $g\text{-C}_3\text{N}_4$ to take part in a reduction reaction, consistent with the direct Z-scheme charge migration mechanism. Meanwhile, the photogenerated holes remain on the (001) facets of the TiO_2 HNBs and take part in an oxidation reaction. As a result, the electron–hole separation across the TiO_2 HNB/ $g\text{-C}_3\text{N}_4$ interface is much faster than that of the TiO_2 NS/ $g\text{-C}_3\text{N}_4$ interface, and the former achieved the highest photocatalytic performance among all the prepared samples for degradation of Brilliant Red X3B (Fig. 17(E) and (F)). This work showed that appropriate interface engineering, which requires careful selection of the facets of each individual semiconductor to be exposed in the assembled direct Z-scheme photocatalyst, can greatly improve the electron–hole separation efficiency. Thus, the photocatalytic performance is enhanced.

4.6. Mass ratio

In the Z-scheme photocatalytic reaction, the photogenerated electrons from the CB of PS II require an equivalent number of photogenerated holes from the VB of PS I to be filled at the solid–solid contact interface. Therefore, the mass ratio between PS II and PS I should be optimized. Otherwise, the two species of photogenerated charge carriers will be imbalanced, and the excess holes or electrons will recombine with their counterparts in the bulk and will not contribute to the Z-scheme photocatalytic reaction. Thus, PS II and PS I should produce the same number of photogenerated charge carriers. Fortunately, this can be achieved by tuning the mass (molar) ratio of PS II and PS I; notably, this ratio will affect the geometric architecture of the PS–PS system [188]. The performance of the photo-

Fig. 17. Schematic illustration of the contact interface between TiO_2 and $g\text{-C}_3\text{N}_4$ of $\text{TiO}_2/g\text{-C}_3\text{N}_4$ (A, B) and $\text{TiO}_2\text{-HNB}/g\text{-C}_3\text{N}_4$ (C). (D) Schematic for the mechanism of photoinduced charge-carrier transfer in $g\text{-C}_3\text{N}_4/\text{TiO}_2\text{-HNB}$ hybrid under UV irradiation. Time dependence of the induced photoluminescence intensity at 450 nm of the photocatalysts (E) and comparison of the corresponding rate constants (F) [186].

catalyst also depends on the rate of photogenerated-charge separation and the nature of the photocatalytic system [188].

Furthermore, Ng et al. [189] have synthesized a Z-scheme photocatalytic system for water splitting composed of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -multiwalled carbon nanotube (MWCNT)- TiO_2 composites by a facile coating and hydrothermal route (Fig. 18(A) and (B)). When the mass ratio of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and TiO_2 is controlled at 1:1, the as-obtained $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -MWCNT- TiO_2 Z-scheme photocatalyst shows the highest photocatalytic activity for hydrogen generation. However, others have reported that the Z-scheme WO_3 - C_3N_4 system shows the highest activity for water splitting when the mass ratio of WO_3 to C_3N_4 is $\sim 1:9$ (Fig. 18(C)–(E)) [190]. The difference in the optimal mass ratios of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}/\text{TiO}_2$ and $\text{WO}_3/\text{C}_3\text{N}_4$ may result from their different geometric architectures. In the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}/\text{TiO}_2$ system, the Z-scheme electron transfer depends on the carbon nanotube connection between $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ and TiO_2 . The PS I-carbon-PS II contact interface does contribute to the Z-scheme electron transfer. However, the contact interfaces between either the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ or TiO_2 particles themselves, that is, either PS II-carbon-PS II or PS I-carbon-PS I, do not contribute to the Z-scheme electron transfer. Thus, an excess of any component in the $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -MWCNT- TiO_2 system will reduce the extent of the PS I-carbon-PS II contact interface, resulting in the deterioration of the charge transfer [99]. In contrast, in the $\text{WO}_3/\text{C}_3\text{N}_4$ system, C_3N_4 is the host and WO_3 is the guest, which is chemically deposited on the surface of the C_3N_4 particles. When the mass ratio of WO_3 to C_3N_4 is much

lower than 1:9, WO_3 is likely to be sparsely dispersed on the C_3N_4 surface. Only a small solid-solid contact interface is formed, and a WO_3 layer will even be formed on the C_3N_4 , which cannot effectively transfer the photogenerated electrons from C_3N_4 to WO_3 . Moreover, a similar argument applies to that which was outlined at the end of the last paragraph. Namely, a significant fraction of the photogenerated charge carriers will recombine in C_3N_4 and WO_3 , resulting in a low utilization efficiency of solar light. Enlarging the solid-solid contact interface between C_3N_4 and WO_3 will provide additional channels for the Z-scheme electron transfer. However, over-raising the mass ratio of C_3N_4 to WO_3 results in a thick C_3N_4 layer on the WO_3 surface. This condition will reduce the penetration of the incident light reaching the WO_3 surface. Consequently, WO_3 photoexcitation will be weakened. In this case, the number of photogenerated charge carriers in WO_3 will be significantly lower than that in C_3N_4 . Besides, the thicker the C_3N_4 layer, the greater the distance for electron transfer from WO_3 to the C_3N_4 surface, thus raising the probability of electron-hole recombination in the bulk. Similar results can be seen in the TiO_2 -CdS and ZnO -CdS systems, wherein CdS is deposited onto the TiO_2 (ZnO) surfaces via a chemical bath, and the optimal mass of CdS in the systems is also smaller than that of TiO_2 (ZnO) [191,192].

5. Conclusions and prospect

Photocatalysis is a promising approach to solve future environmental and energy problems. As such, considerable effort

Fig. 18. (A) Schematic of $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -MWCNT- TiO_2 nanocomposites. (B) Proposed electron/hole transfer mechanism for MWCNT-mediated Z-scheme $\text{Zn}_{0.5}\text{Cd}_{0.5}\text{S}$ -MWCNT- TiO_2 system [189]. (C) Schematic of the functional mechanism of g- C_3N_4 / WO_3 composites. C_3N_4 is the host, and WO_3 is the guest. (D) Schematic of the direct Z-scheme electron transfer from WO_3 to g- C_3N_4 . (E) Comparison of average photocatalytic H_2 production rates of GWx composites (GW stands for g- C_3N_4 / WO_3 composites, where x indicates the amount of WO_3 (in mg) used in preparing the composite), and pure g- C_3N_4 samples loaded with 1 wt% Pt cocatalyst for the first 3 h under simulated solar irradiation [190].

has been devoted to photocatalyst development. Their practical utility depends on the development of efficient, stable, and low-cost photocatalysts. However, these requirements are difficult to satisfy simultaneously with single-component photocatalysts. Z-scheme photocatalytic systems extend the utilization range of visible light, improve the separation/transport of charge carriers, and substantially enhance the efficiency of photocatalytic activities. TiO₂-based Z-scheme photocatalytic systems exhibit good properties for photolysis and thus have received widespread attention. Direct Z-scheme TiO₂ photocatalysts show great potential for various photocatalytic applications ranging from environmental remediation, such as CO₂ reduction and organic-compound decomposition, to solar fuel production, such as water splitting.

Great progress has been achieved in research on TiO₂-based Z-scheme systems. However, the development of direct Z-scheme TiO₂-based photocatalysts is still in its early stage, and challenges remain. Photocatalytic reactions are complex, and many important aspects remain to be fully understood. In this regard, the following four key issues should be further clarified.

(1) The mechanisms of Z-scheme photocatalysts and related processes, such as charge-carrier transfer and photocatalytic reaction pathways, should be more comprehensively understood. The combination of experiments with theoretical calculations may be an effective strategy. A range of characterization methods, such as photocatalytic testing, radical-species trapping tests, X-ray photoelectron spectroscopy, transient time-resolved luminescence decay measurements, and surface photovoltaic techniques, are available to help elucidate the photocatalytic processes.

(2) The contact interface between the two semiconductors in Z-scheme photocatalysts must be rationally controlled and optimized. An effective charge-carrier separation across the interface is necessary to optimize the photocatalytic performance of a direct Z-scheme photocatalyst. The counterpart for the all-solid-state Z-scheme photocatalyst, the redox mediators, or the solid-state electron mediators of the system may also play an important role in charge-carrier transport. Thus, new redox mediators or solid-state electron mediators that can suppress the backward reaction and improve light transmission should be developed.

(3) New Z-scheme photocatalytic systems with ternary or multicomponent structures can be created by depositing suitable cocatalysts for oxidation and reduction on the PS I and PS II surfaces of direct Z-scheme photocatalysts, consequently enhancing the electron-hole separation efficiency. One approach to designing such novel hybrid catalysts could be to select photocatalytic materials that simulate photosynthetic proteins.

(4) The inhibition of the reverse reaction and the enhancement of catalyst recycling are further challenges in the use of Z-scheme photocatalysts. In a photocatalytic water splitting system, PS I produces hydrogen, while PS II yields oxygen. Therefore, these products should be efficiently separated and collected. Another problem is photocatalyst recycling. TiO₂ photocatalysts usually exist in the form of powder and are dispersed in solution, which complicates their recycling after the

photocatalytic reaction. For industrial production, TiO₂ photocatalysts must be capable of efficient repeated use without loss of effectiveness. Thus, the problems associated with catalyst recycling must be urgently solved.

Although the photoelectric conversion efficiency of Z-scheme TiO₂ photocatalytic systems currently remains low, such systems are nonetheless promising. The creation of TiO₂-based Z-scheme photocatalysts that simulate natural photosynthesis to harvest solar energy will greatly stimulate advances in energy conversion and environmental remediation. We hope that this rapidly developing field of Z-scheme photocatalysis will enable a breakthrough in industrialization and contribute to the sustainable development of human society.

References

- [1] S. Chu, A. Majumdar, *Nature*, **2012**, 488, 294–303.
- [2] N. S. Lewis, D. G. Nocera, *Proc. Natl. Acad. Sci. USA*, **2006**, 103, 15729–15735.
- [3] N. S. Lewis, *Science*, **2016**, 351, aad1920.
- [4] A. Fujishima, K. Honda, *Nature*, **1972**, 238, 37–38.
- [5] J. Q. Wen, X. Li, W. Liu, Y. P. Fang, J. Xie, Y. H. Xu, *Chin. J. Catal.*, **2015**, 36, 2049–2070.
- [6] L. Chen, J. He, Y. Liu, P. Chen, C. T. Au, S. F. Yin, *Chin. J. Catal.*, **2016**, 37, 780–791.
- [7] W. L. Yu, J. Zhang, T. Peng, *Appl. Catal. B*, **2016**, 181, 220–227.
- [8] C. P. Sajjan, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, S. W. Cao, *Nano Res.*, **2015**, 9, 3–27.
- [9] H. Du, Y. N. Liu, C. C. Shen, A. W. Xu, *Chin. J. Catal.*, **2017**, 38, 1295–1306.
- [10] D. Li, W. D. Shi, *Chin. J. Catal.*, **2016**, 37, 792–799.
- [11] K. Z. Qi, F. Zasada, W. Piskorz, P. Indyka, J. Gryboś, M. Trochowski, M. Buchalska, M. Kobielski, W. Macyk, Z. Sojka, *J. Phys. Chem. C*, **2016**, 120, 5442–5456.
- [12] H. Park, H. I. Kim, G. H. Moon, W. Choi, *Energy Environ. Sci.*, **2016**, 9, 411–433.
- [13] W. P. Zhang, X. Y. Xiao, Y. Li, X. Y. Zeng, L. L. Zheng, C. X. Wan, *Appl. Surf. Sci.*, **2016**, 389, 496–506.
- [14] W. Y. Dong, Y. W. Yao, Y. J. Sun, W. M. Hua, G. S. Zhuang, *Chin. J. Catal.*, **2016**, 37, 846–854.
- [15] Y. X. Liu, Z. L. Wang, W. X. Huang, *Appl. Surf. Sci.*, **2016**, 389, 760–767.
- [16] W. L. Yu, D. F. Xu, T. Y. Peng, *J. Mater. Chem. A*, **2015**, 3, 19936–19947.
- [17] Y. N. Liu, R. X. Wang, Z. K. Yang, H. Du, Y. F. Jiang, C. C. Shen, K. Liang, A. W. Xu, *Chin. J. Catal.*, **2015**, 36, 2135–2144.
- [18] K. Z. Qi, B. Cheng, J. G. Yu, W. Ho, *J. Alloys Compd.*, **2017**, 727, 792–820.
- [19] J. J. Kong, X. D. Lai, Z. B. Rui, H. B. Ji, S. F. Ji, *Chin. J. Catal.*, **2016**, 37, 869–877.
- [20] S. S. Wu, H. Q. Cao, S. F. Yin, X. W. Liu, X. R. Zhang, *J. Phys. Chem. C*, **2009**, 113, 17893–17898.
- [21] G. X. Zhou, X. L. Wu, L. Z. Liu, X. B. Zhu, X. S. Zhu, Y. L. Hao, P. K. Chu, *Appl. Surf. Sci.*, **2015**, 349, 798–804.
- [22] J. Wei, S. L. Xue, P. Xie, R. J. Zou, *Appl. Surf. Sci.*, **2016**, 376, 172–179.
- [23] N. Shanmugam, T. Sathya, G. Viruthagiri, C. Kalyanasundaram, R. Gobi, S. Ragupathy, *Appl. Surf. Sci.*, **2016**, 360, 283–290.
- [24] J. Wei, S. Xue, P. Xie, R. Zou, *Appl. Surf. Sci.*, **2016**, 376, 172–179.

Graphical Abstract

Chin. J. Catal., 2017, 38: 1936–1955 doi: 10.1016/S1872-2067(17)62962-0

A review on TiO₂-based Z-scheme photocatalysts

Kezhen Qi, Bei Cheng, Jiaguo Yu *, Wingkei Ho *

Wuhan University of Technology, China; Shenyang Normal University, China; The Education University of Hong Kong, China; King Abdulaziz University, Saudi Arabia

TiO₂-based Z-scheme photocatalysts are reviewed in this paper about the reaction mechanism, the recent research progress in application, the methods for enhancing the photocatalytic performance, and the perspective on challenges and future developments.

- [25] O. Mehraj, B. M. Pirzada, N. A. Mir, M. Z. Khan, S. Sabir, *Appl. Surf. Sci.*, **2016**, 387, 642–651.
- [26] S. G. Hosseini, S. Safshekan, *Chin. J. Catal.*, **2017**, 38, 710–716.
- [27] H. L. Tan, R. Amal, Y. H. Ng, *J. Mater. Chem. A*, **2017**, 5, 16498–16521.
- [28] R. A. He, S. W. Cao, P. Zhou, J. G. Yu, *Chin. J. Catal.*, **2014**, 35, 989–1007.
- [29] G. S. Zhao, W. Liu, J. Y. Li, Q. Y. Lv, W. X. Li, L. T. Liang, *Appl. Surf. Sci.*, **2016**, 390, 531–539.
- [30] L. Chen, J. He, Y. Liu, P. Chen, C. T. Au, S. F. Yin, *Chin. J. Catal.*, **2016**, 37, 780–791.
- [31] Y. Y. Luo, G. Q. Tan, G. H. Dong, H. J. Ren, A. Xia, *Appl. Surf. Sci.*, **2016**, 364, 156–165.
- [32] K. Z. Qi, H. S. Qi, J. Q. Yang, G. C. Wang, R. Selvaraj, W. Zheng, *Chem. Eng. J.*, **2017**, 324, 347–357.
- [33] Y. H. Cheng, Y. J. Lin, J. P. Xu, J. He, T. Z. Wang, G. J. Yu, D. W. Shao, W. H. Wang, F. Lu, L. Li, X. W. Du, W. C. Wang, H. Liu, R. K. Zheng, *Appl. Surf. Sci.*, **2016**, 366, 120–128.
- [34] L. Liu, L. Ding, Y. G. Liu, W. J. An, S. L. Lin, Y. H. Liang, W. Q. Cui, *Appl. Surf. Sci.*, **2016**, 364, 505–515.
- [35] M. Nishikawa, M. Fukuda, Y. Nakabayashi, N. Saito, N. Ogawa, T. Nakajima, K. Shinoda, T. Tsuchiya, Y. Nosaka, *Appl. Surf. Sci.*, **2016**, 363, 173–180.
- [36] X. P. Qiu, J. S. Yu, H. M. Xu, W. X. Chen, W. Hu, G. L. Chen, *Appl. Surf. Sci.*, **2016**, 382, 249–259.
- [37] J. Jin, J. G. Yu, D. P. Guo, C. Cui, W. Ho, *Small*, **2015**, 11, 5262–5271.
- [38] H. Sun, B. H. Dong, G. Su, R. J. Gao, W. Liu, L. Song, L. X. Cao, *Appl. Surf. Sci.*, **2015**, 343, 181–187.
- [39] A. Arfaoui, S. Touihri, A. Mhamdi, A. Labidi, T. Manoubi, *Appl. Surf. Sci.*, **2015**, 357, 1089–1096.
- [40] P. Y. Dong, G. H. Hou, X. G. Xi, R. Shao, F. Dong, *Environ. Sci. Nano*, **2017**, 4, 539–557.
- [41] R. G. Li, *Chin. J. Catal.*, **2017**, 38, 5–12.
- [42] L. Pan, J. W. Zhang, X. Jia, Y. H. Ma, X. W. Zhang, L. Wang, J. J. Zou, *Chin. J. Catal.*, **2017**, 38, 253–259.
- [43] J. X. Low, B. Cheng, J. G. Yu, *Appl. Surf. Sci.*, **2017**, 392, 658–686.
- [44] Y. S. Liu, G. B. Ji, M. A. Dastageer, L. Zhu, J. Y. Wang, B. Zhang, X. F. Chang, M. A. Gondal, *RSC Adv.*, **2014**, 4, 56961–56969.
- [45] J. W. Fu, B. C. Zhu, C. J. Jiang, B. Cheng, W. You, J. G. Yu, *Small*, **2017**, 13, 1603938.
- [46] K. Li, B. S. Peng, T. Y. Peng, *ACS Catal.*, **2016**, 6, 7485–7527.
- [47] S. R. Lingampalli, M. M. Ayyub, C. N. R. Rao, *ACS Omega*, **2017**, 2, 2740–2748.
- [48] T. M. Di, B. C. Zhu, B. Cheng, J. G. Yu, J. S. Xu, *J. Catal.*, **2017**, 352, 532–541.
- [49] F. Wang, Y. Zhou, P. Li, L. Kuai, Z. G. Zou, *Chin. J. Catal.*, **2016**, 37, 863–868.
- [50] H. H. Li, X. Y. Wu, S. Yin, K. Katsumata, Y. H. Wang, *Appl. Surf. Sci.*, **2017**, 392, 531–539.
- [51] D. Wang, X. Y. Pan, G. T. Wang, Z. G. Yi, *RSC Adv.*, **2015**, 5, 22038–22043.
- [52] Y. Zhao, X. Huang, X. Tan, T. Yu, X. L. Li, L. B. Yang, S. C. Wang, *Appl. Surf. Sci.*, **2016**, 365, 209–217.
- [53] W. K. Jo, T. Adinaveen, J. J. Vijaya, N. C. S. Selvam, *RSC Adv.*, **2016**, 6, 10487–10497.
- [54] J. Xing, Z. P. Chen, F. Y. Xiao, X. Y. Ma, C. Z. Wen, Z. Li, H. G. Yang, *Chem. Asian J.*, **2013**, 8, 1265–1270.
- [55] M. N. Huang, J. H. Yu, Q. Hu, W. L. Su, M. G. Fan, B. Li, L. H. Dong, *Appl. Surf. Sci.*, **2016**, 389, 1084–1093.
- [56] W. K. Jo, T. Sivakumar Natarajan, *ACS Appl. Mater. Interfaces*, **2015**, 7, 17138–17154.
- [57] Y. Sohn, W. X. Huang, F. Taghipour, *Appl. Surf. Sci.*, **2017**, 396, 1696–1711.
- [58] M. Y. Wang, J. Ioccozia, L. Sun, C. J. Lin, Z. Q. Lin, *Energy Environ.*

- Sci.*, **2014**, 7, 2182–2202.
- [59] Z. Y. Huang, Z. G. Gao, S. M. Gao, Q. Y. Wang, Z. Y. Wang, B. B. Huang, Y. Dai, *Chin. J. Catal.*, **2017**, 38, 821–830.
- [60] W. J. Liao, M. Murugananthan, Y. R. Zhang, *Phys. Chem. Chem. Phys.*, **2015**, 17, 8877–8884.
- [61] M. S. Akple, J. X. Low, S. W. Liu, B. Cheng, J. G. Yu, W. Ho, *J. CO₂ Utilization*, **2016**, 16, 442–449.
- [62] E. Shin, S. Jin, J. Kim, S. J. Chang, B. H. Jun, K. W. Park, J. Hong, *Appl. Surf. Sci.*, **2016**, 379, 33–38.
- [63] M. S. Akple, J. X. Low, Z. Qin, S. Wageh, A. A. Al-Ghamdi, J. G. Yu, S. W. Liu, *Chin. J. Catal.*, **2015**, 36, 2127–2134.
- [64] Y. Du, D. P. Tang, G. K. Zhang, X. Y. Wu, *Chin. J. Catal.*, **2015**, 36, 2219–2228.
- [65] M. C. Wen, S. S. Zhang, W. R. Dai, G. S. Li, D. Q. Zhang, *Chin. J. Catal.*, **2015**, 36, 2095–2102.
- [66] S. A. Bakar, C. Ribeiro, *Appl. Surf. Sci.*, **2016**, 377, 121–133.
- [67] L. Gomathi Devi, R. Kavitha, *Appl. Surf. Sci.*, **2016**, 360, 601–622.
- [68] K. Tahir, A. Ahmad, B. Li, S. Nazir, A. Ullah Khan, T. Nasir, Z. Ul Haq Khan, R. Naz, M. Raza, *J. Photochem. Photobiol. B*, **2016**, 162, 189–198.
- [69] X. F. Zhu, B. Cheng, J. G. Yu, W. Ho, *Appl. Surf. Sci.*, **2016**, 364, 808–814.
- [70] X. F. Wang, R. Yu, K. Wang, G. Q. Yang, H. G. Yu, *Chin. J. Catal.*, **2015**, 36, 2211–2218.
- [71] C. Jin, Y. Dai, W. Wei, X. C. Ma, M. M. Li, B. B. Huang, *Appl. Surf. Sci.*, **2017**, 426, 639–646.
- [72] M. Nischk, P. Mazierski, Z. Wei, K. Siuzdak, N. A. Kouame, E. Kowalska, H. Remita, A. Zaleska-Medynska, *Appl. Surf. Sci.*, **2016**, 387, 89–102.
- [73] Y. C. Yao, X. R. Dai, X. Y. Hu, S. Z. Huang, Z. Jin, *Appl. Surf. Sci.*, **2016**, 387, 469–476.
- [74] M. Klein, J. Nadolna, A. Gołbiewska, P. Mazierski, T. Klimczuk, H. Remita, A. Zaleska-Medynska, *Appl. Surf. Sci.*, **2016**, 378, 37–48.
- [75] G. K. Zhang, H. Wang, S. Guo, J. T. Wang, J. Liu, *Appl. Surf. Sci.*, **2016**, 362, 257–264.
- [76] Q. Wang, Z. N. Qin, J. Chen, B. S. Ren, Q. F. Chen, Y. C. Guo, X. F. Cao, *Appl. Surf. Sci.*, **2016**, 364, 1–8.
- [77] X. Fu, L. J. Pan, S. Li, Q. Wang, J. Qin, Y. Y. Huang, *Appl. Surf. Sci.*, **2016**, 363, 412–420.
- [78] T. T. Yu, L. F. Liu, F. L. Yang, *Chin. J. Catal.*, **2017**, 38, 270–277.
- [79] K. Ma, O. Yehezkeli, D. W. Domaille, H. H. Funke, J. N. Cha, *Angew. Chem. Int. Ed.*, **2015**, 54, 11490–11494.
- [80] J. Li, M. Zhang, X. Li, Q. Y. Li, J. J. Yang, *Appl. Catal. B*, **2017**, 212, 106–114.
- [81] Y. F. Li, W. P. Zhang, X. Shen, P. F. Peng, L. B. Xiong, Y. Yu, *Chin. J. Catal.*, **2015**, 36, 2229–2236.
- [82] Y. Y. Lu, Y. Y. Zhang, J. Zhang, Y. Shi, Z. Li, Z. C. Feng, C. Li, *Appl. Surf. Sci.*, **2016**, 370, 312–319.
- [83] X. J. Zou, Y. Y. Dong, X. D. Zhang, Y. B. Cui, *Appl. Surf. Sci.*, **2016**, 366, 173–180.
- [84] D. Wang, Y. Xu, F. Sun, Q. H. Zhang, P. Wang, X. Y. Wang, *Appl. Surf. Sci.*, **2016**, 377, 221–227.
- [85] H. B. Feng, Y. P. Li, D. M. Luo, G. R. Tan, J. B. Jiang, H. H. Yuan, S. J. Peng, D. Qian, *Chin. J. Catal.*, **2016**, 37, 855–862.
- [86] K. Z. Qi, R. Selvaraj, T. Al Fahdi, S. Al-Kindy, Y. Kim, G. C. Wang, C. W. Tai, M. Sillanpää, *Appl. Surf. Sci.*, **2016**, 387, 750–758.
- [87] Y. H. Su, P. Chen, F. L. Wang, Q. X. Zhang, T. S. Chen, Y. F. Wang, K. Yao, W. Y. Lv, G. G. Liu, *RSC Adv.*, **2017**, 7, 34096–34103.
- [88] A. L. Qu, H. L. Xie, X. M. Xu, Y. Y. Zhang, S. W. Wen, Y. F. Cui, *Appl. Surf. Sci.*, **2016**, 375, 230–241.
- [89] M. Shanmugam, A. Alsalmeh, A. Alghamdi, R. Jayavel, *J. Photochem. Photobiol. B*, **2016**, 163, 216–223.
- [90] D. Hazarika, N. Karak, *Appl. Surf. Sci.*, **2016**, 376, 276–285.
- [91] J. G. Yu, T. T. Ma, G. Liu, B. Cheng, *Dalton Trans.*, **2011**, 40, 6635–6644.
- [92] Y. F. Yang, Z. Ma, L. D. Xu, H. F. Wang, N. Fu, *Appl. Surf. Sci.*, **2016**, 369, 576–583.
- [93] H. L. Wang, L. S. Zhang, Z. G. Chen, J. Q. Hu, S. J. Li, Z. H. Wang, J. S. Liu, X. C. Wang, *Chem. Soc. Rev.*, **2014**, 43, 5234–5244.
- [94] W. W. Zhang, H. L. Guo, H. Q. Sun, R. C. Zeng, *Appl. Surf. Sci.*, **2016**, 382, 128–134.
- [95] W. K. Wang, D. F. Xu, B. Cheng, J. G. Yu, C. J. Jiang, *J. Mater. Chem. A*, **2017**, 5, 5020–5029.
- [96] W. P. Zhang, X. Y. Xiao, L. L. Zheng, C. X. Wan, *Appl. Surf. Sci.*, **2015**, 358, 468–478.
- [97] A. Y. Meng, J. Zhang, D. F. Xu, B. Cheng, J. G. Yu, *Appl. Catal. B Environ.*, **2016**, 198, 286–294.
- [98] J. X. Low, J. G. Yu, M. Jaroniec, S. Wageh, A. A. Al-Ghamdi, *Adv. Mater.*, **2017**, 29, 1601694.
- [99] P. Zhou, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2014**, 26, 4920–4935.
- [100] A. Kudo, *MRS Bull.*, **2011**, 36, 32–38.
- [101] H. Kato, M. Hori, R. Kenta, Y. Shimodaira, A. Kudo, *Chem. Lett.*, **2004**, 33, 1348–1349.
- [102] S. Sato, T. Arai, T. Morikawa, K. Uemura, T. M. Suzuki, H. Tanaka, T. Kajino, *J. Am. Chem. Soc.*, **2011**, 133, 15240–15243.
- [103] E. N. K. Glover, S. G. Ellington, G. Sankar, R. G. Palgrave, *J. Mater. Chem. A*, **2016**, 4, 6946–6954.
- [104] B. C. Zhu, P. F. Xia, Y. Li, W. Ho, J. G. Yu, *Appl. Surf. Sci.*, **2017**, 391, 175–183.
- [105] H. Tang, Y. H. Fu, S. F. Chang, S. Y. Xie, G. G. Tang, *Chin. J. Catal.*, **2017**, 38, 337–347.
- [106] T. B. Nguyen, R. A. Doong, *RSC Adv.*, **2016**, 6, 103428–103437.
- [107] L. F. Cui, X. Ding, Y. G. Wang, H. C. Shi, L. H. Huang, Y. Zuo, S. F. Kang, *Appl. Surf. Sci.*, **2017**, 391, 202–210.
- [108] M. E. Aguirre, R. X. Zhou, A. J. Eugene, M. I. Guzman, M. A. Grela, *Appl. Catal. B*, **2017**, 217, 485–493.
- [109] J. Li, M. Zhang, Q. Y. Li, J. J. Yang, *Appl. Surf. Sci.*, **2017**, 391, 184–193.
- [110] D. F. Xu, B. Cheng, S. W. Cao, J. G. Yu, *Appl. Catal. B*, **2015**, 164, 380–388.
- [111] S. Q. Song, A. Y. Meng, S. J. Jiang, B. Cheng, C. J. Jiang, *Appl. Surf. Sci.*, **2017**, 396, 1368–1374.
- [112] J. X. Low, C. J. Jiang, B. Cheng, S. Wageh, A. A. Al-Ghamdi, J. Yu, *Small Methods*, **2017**, 1, 1700080.
- [113] Y. Tachibana, L. Vayssieres, J. R. Durrant, *Nat. Photonics*, **2012**, 6, 511–518.
- [114] J. L. Herek, W. Wohlleben, R. J. Cogdell, D. Zeidler, M. Motzkus, *Nature*, **2002**, 417, 533–535.
- [115] R. Abe, K. Sayama, H. Sugihara, *J. Phys. Chem. B*, **2005**, 109, 16052–16061.
- [116] H. J. Li, Y. Zhou, W. G. Tu, J. H. Ye, Z. G. Zou, *Adv. Funct. Mater.*, **2015**, 25, 998–1013.
- [117] R. Abe, K. Shinmei, N. Koumura, K. Hara, B. Ohtani, *J. Am. Chem. Soc.*, **2013**, 135, 16872–16884.
- [118] Y. Sasaki, A. Iwase, H. Kato, A. Kudo, *J. Catal.*, **2008**, 259, 133–137.
- [119] K. Maeda, *ACS Catal.*, **2013**, 3, 1486–1503.
- [120] Y. Sasaki, H. Kato, A. Kudo, *J. Am. Chem. Soc.*, **2013**, 135, 5441–5449.
- [121] K. Sayama, R. Abe, H. Arakawa, H. Sugihara, *Catal. Commun.*, **2006**, 7, 96–99.
- [122] A. J. Bard, *J. Photochem.*, **1979**, 10, 59–75.
- [123] H. Tada, T. Mitsui, T. Kiyonaga, T. Akita, K. Tanaka, *Nat. Mater.*, **2006**, 5, 782–786.

- [124] H. J. Yun, H. Lee, N. D. Kim, D. M. Lee, S. Yu, J. Yi, *ACS Nano*, **2011**, 5, 4084–4090.
- [125] F. J. Wu, X. Li, W. Liu, S. T. Zhang, *Appl. Surf. Sci.*, **2017**, 405, 60–70.
- [126] J. T. Li, S. K. Cushing, P. Zheng, T. Senty, F. Meng, A. D. Bristow, A. Manivannan, N. Q. Wu, *J. Am. Chem. Soc.*, **2014**, 136, 8438–8449.
- [127] S. T. Kochuveedu, Y. H. Jang, D. H. Kim, *Chem. Soc. Rev.*, **2013**, 42, 8467–8493.
- [128] K. E. Byun, H. J. Chung, J. Lee, H. Yang, H. J. Song, J. Heo, D. H. Seo, S. Park, S. W. Hwang, I. Yoo, K. Kim, *Nano Lett.*, **2013**, 13, 4001–4005.
- [129] J. G. Yu, S. H. Wang, J. X. Low, W. Xiao, *Phys. Chem. Chem. Phys.*, **2013**, 15, 16883–16890.
- [130] A. Y. Meng, B. C. Zhu, B. Zhong, L. Y. Zhang, B. Cheng, *Appl. Surf. Sci.*, **2017**, 422, 518–527.
- [131] J. Q. Wen, J. Xie, X. B. Chen, X. Li, *Appl. Surf. Sci.*, **2017**, 391, 72–123.
- [132] Z. H. Xi, C. J. Li, L. Zhang, M. Y. Xing, J. L. Zhang, *Int. J. Hydrogen Energy*, **2014**, 39, 6345–6353.
- [133] Y. Zheng, Z. M. Pan, X. C. Wang, *Chin. J. Catal.*, **2013**, 34, 524–535.
- [134] S. W. Cao, J. X. Low, J. G. Yu, M. Jaroniec, *Adv. Mater.*, **2015**, 27, 2150–2176.
- [135] T. T. Wu, X. D. Kang, M. W. Kadi, I. Ismail, G. Liu, H. M. Cheng, *Chin. J. Catal.*, **2015**, 36, 2103–2108.
- [136] M. A. Mahadik, G. W. An, S. David, S. H. Choi, M. Cho, J. S. Jang, *Appl. Surf. Sci.*, **2017**, 426, 833–843.
- [137] J. W. Fu, J. G. Yu, C. Jiang, B. Cheng, *Adv. Energy Mater.*, **2017**, 7, 1701503.
- [138] T. V. M. Sreekanth, J. J. Shim, Y. R. Lee, *J. Photochem. Photobiol. B*, **2017**, 169, 90–95.
- [139] Y. Liu, Y. D. Shi, X. Liu, H. X. Li, *Appl. Surf. Sci.*, **2017**, 396, 58–66.
- [140] J. Mac Mahon, S. C. Pillai, J. M. Kelly, L. W. Gill, *J. Photochem. Photobiol. B*, **2017**, 170, 79–90.
- [141] S. Y. Wang, X. L. Yang, X. H. Zhang, X. Ding, Z. X. Yang, K. Dai, H. Chen, *Appl. Surf. Sci.*, **2017**, 391, 194–201.
- [142] S. J. Yu, S. Y. Lee, J. Yeo, J. W. Han, J. Yi, *J. Phys. Chem. C*, **2014**, 118, 29583–29590.
- [143] H. Zhao, M. Wu, J. Liu, Z. Deng, Y. Li, B. L. Su, *Appl. Catal. B*, **2016**, 184, 182–190.
- [144] F. Y. Xu, W. Xiao, B. Cheng, J. G. Yu, *Int. J. Hydrogen Energy*, **2014**, 39, 15394–15402.
- [145] Y. C. Wei, J. Q. Jiao, Z. Zhao, J. Liu, J. M. Li, G. Y. Jiang, Y. J. Wang, A. J. Duan, *Appl. Catal. B Environ.*, **2015**, 179, 422–432.
- [146] B. Y. Bai, Q. Qiao, J. H. Li, J. M. Hao, *Chin. J. Catal.*, **2016**, 37, 102–122.
- [147] J. J. Liu, B. Cheng, J. G. Yu, *Phys. Chem. Chem. Phys.*, **2016**, 18, 31175–31183.
- [148] A. A. Essawy, S. M. Sayyah, A. M. El-Nggar, *J. Photochem. Photobiol. B*, **2017**, 173, 170–180.
- [149] T. Chen, S. W. Yu, X. X. Fang, H. H. Huang, L. Li, X. Y. Wang, H. H. Wang, *Appl. Surf. Sci.*, **2016**, 389, 303–310.
- [150] N. Tian, H. W. Huang, Y. He, Y. X. Guo, T. R. Zhang, Y. H. Zhang, *Dalton Trans.*, **2015**, 44, 4297–4307.
- [151] K. P. Xie, Q. Wu, Y. Y. Wang, W. W. Guo, M. Y. Wang, L. Sun, C. J. Lin, *Electrochem. Commun.*, **2011**, 13, 1469–1472.
- [152] Y. Sasaki, H. Nemoto, K. Saito, A. Kudo, *J. Phys. Chem. C*, **2009**, 40, 17536–17542.
- [153] Y. Xu, M. A. A. Schoonen, *Am. Mineral.*, **2000**, 85, 543–556.
- [154] C. Guillard, H. Lachheb, A. Houas, M. Ksibi, E. Elaloui, J. M. Herrmann, *J. Photochem. Photobiol. A*, **2003**, 158, 27–36.
- [155] Z. F. Huang, L. Pan, J. J. Zou, X. W. Zhang, L. Wang, *Nanoscale*, **2014**, 6, 14044–14063.
- [156] Q. X. Jia, A. Iwase, A. Kudo, *Chem. Sci.*, **2014**, 5, 1513–1519.
- [157] M. Miyauchi, Y. Nukui, D. Atarashi, E. Sakai, *ACS Appl. Mater. Interfaces*, **2013**, 5, 9770–9776.
- [158] H. M. Zhu, B. F. Yang, J. Xu, Z. P. Fu, M. W. Wen, T. Guo, S. Q. Fu, J. Zuo, S. Y. Zhang, *Appl. Catal. B*, **2009**, 90, 463–469.
- [159] S. H. Shen, L. J. Guo, X. B. Chen, F. Ren, C. X. Kronawitter, S. S. Mao, *Int. J. Green Nanotechnol.*, **2010**, 1, M94–M104.
- [160] S. Halas, T. Durakiewicz, *J. Phys.*, **1998**, 10, 10815–10826.
- [161] A. Iwase, Y. H. Ng, Y. Ishiguro, A. Kudo, R. Amal, *J. Am. Chem. Soc.*, **2011**, 133, 11054–11057.
- [162] W. K. Jo, N. C. S. Selvam, *Chem. Eng. J.*, **2017**, 317, 913–924.
- [163] L. B. Kuai, Y. Zhou, W. G. Tu, P. Li, H. J. Li, Q. F. Xu, L. Tang, X. Y. Wang, M. Xiao, Z. G. Zou, *RSC Adv.*, **2015**, 5, 88409–88413.
- [164] L. X. Chen, F. He, N. Q. Zhao, R. S. Guo, *Appl. Surf. Sci.*, **2017**, 420, 669–680.
- [165] P. Li, Y. Zhou, H. J. Li, Q. F. Xu, X. G. Meng, X. Y. Wang, M. Xiao, Z. G. Zou, *Chem. Commun.*, **2015**, 51, 800–803.
- [166] K. Iwashina, A. Iwase, Y. H. Ng, R. Amal, A. Kudo, *J. Am. Chem. Soc.*, **2015**, 137, 604–607.
- [167] T. Takayama, K. Sato, T. Fujimura, Y. Kojima, A. Iwase, A. Kudo, *Faraday Discuss.*, **2017**, 198, 397–407.
- [168] H. Q. Gao, P. Zhang, J. H. Hu, J. M. Pan, J. J. Fan, G. S. Shao, *Appl. Surf. Sci.*, **2017**, 391, 211–217.
- [169] B. J. Ma, J. S. Kim, C. H. Choi, S. I. Woo, *Int. J. Hydrogen Energy*, **2013**, 38, 3582–3587.
- [170] W. P. Zhang, X. Y. Xiao, X. Y. Zeng, Y. Li, L. L. Zheng, C. X. Wan, *J. Alloys Compd.*, **2016**, 685, 774–783.
- [171] J. H. Hu, L. J. Wang, P. Zhang, C. H. Liang, G. S. Shao, *J. Power Sources*, **2016**, 328, 28–36.
- [172] W. K. Jo, T. Adinaveen, J. J. Vijayab, N. C. S. Selvam, *RSC Adv.*, **2016**, 6, 10487–10497.
- [173] H. Q. Gao, P. Zhang, J. T. Zhao, Y. S. Zhang, J. H. Hu, G. S. Shao, *Appl. Catal. B*, **2017**, 210, 297–305.
- [174] R. Asahi, T. Morikawa, T. Ohwaki, K. Aoki, Y. Taga, *Science*, **2001**, 293, 269–271.
- [175] J. Y. Lee, W. K. Jo, *J. Hazard. Mater.*, **2016**, 314, 22–31.
- [176] M. Y. Li, H. Liu, T. T. Liu, Y. X. Qin, *Mater. Charact.*, **2017**, 124, 136–144.
- [177] M. I. Litter, J. A. Navfo, *J. Photochem. Photobiol. A*, **1996**, 98, 171–181.
- [178] K. Kondo, N. Murakami, C. Ye, T. Tsubota, T. Ohno, *Appl. Catal. B*, **2013**, 142–143, 362–367.
- [179] W. K. Jo, T. S. Natarajan, *Chem. Eng. J.*, **2015**, 281, 549–565.
- [180] J. J. Xian, D. Z. Li, J. Chen, X. F. Li, M. He, Y. Shao, L. H. Yu, J. L. Fang, *ACS Appl. Mater. Interfaces*, **2014**, 6, 13157–13166.
- [181] H. Liu, S. Liu, Z. L. Zhang, X. N. Dong, T. T. Liu, *Sci. Rep.*, **2016**, 6, 33839.
- [182] A. Radtke, P. Piszczek, A. Topolski, Ż. Lewandowska, E. Talik, I. H. Andersen, L. P. Nielsen, M. Heikkilä, M. Leskelä, *Appl. Surf. Sci.*, **2016**, 368, 165–172.
- [183] Y. C. Wei, J. Q. Jiao, Z. Zhao, W. J. Zhong, J. Li, J. M. Liu, G. Y. Jiang, A. J. Duan, *J. Mater. Chem. A*, **2015**, 3, 11074–11085.
- [184] B. H. Chen, P. R. Li, S. S. Zhang, W. Zhang, X. P. Dong, F. N. Xi, J. Y. Liu, *J. Colloid Interface Sci.*, **2016**, 478, 263–270.
- [185] L. Ding, H. Zhou, S. Lou, J. Ding, D. Zhang, H. X. Zhu, T. X. Fan, *Int. J. Hydrogen Energy*, **2013**, 38, 8244–8253.
- [186] Z. A. Huang, Q. Sun, K. Lv, Z. Zhang, M. Li, B. Li, *Appl. Catal. B*, **2015**, 164, 420–427.
- [187] J. G. Yu, J. X. Low, W. Xiao, P. Zhou, M. Jaroniec, *J. Am. Chem. Soc.*, **2014**, 136, 8839–8842.
- [188] Y. Li, P. F. Wang, C. P. Huang, W. F. Yao, Q. Wu, Q. J. Xu, *Appl. Catal. B*, **2017**, 205, 489–497.

- [189] B. J. Ng, L. K. Putri, L. L. Tan, P. Pasbakhsh, S. P. Chai, *Chem. Eng. J.*, **2017**, 316, 41–49.
- [190] W. L. Yu, J. X. Chen, T. T. Shang, L. F. Chen, L. Gu, T. Y. Peng, *Appl. Catal. B*, **2017**, 219, 693–704.
- [191] X. W. Wang, G. Liu, Z. G. Chen, F. Z. Li, L. Wang, G. Q. Lu, H. M. Cheng, *Chem. Commun.*, **2009**, 3452–3454.
- [192] X. W. Wang, G. Liu, L. Z. Wang, J. Pan, G. Q. Lu, H. M. Cheng, *J. Mater. Chem.*, **2011**, 21, 869–873.

二氧化钛基Z型光催化剂综述

戚克振^{a,b}, 程 蓓^a, 余家国^{a,d,*}, Wingkei Ho^{c,#}

^a武汉理工大学材料复合新技术国家重点实验室, 湖北武汉430070, 中国

^b沈阳师范大学化学化工学院, 辽宁沈阳110034, 中国

^c香港教育大学科学与环境学系, 香港, 中国

^d沙特阿卜杜勒阿齐兹国王大学科学部物理系, 吉达21589, 沙特阿拉伯

摘要: TiO₂具有无毒、耐腐蚀、高稳定和低成本等特点, 已被广泛应用于光催化领域。然而, TiO₂的禁带较宽, 只能吸收仅占太阳光4%的紫外光部分, 从而严重限制了TiO₂光催化材料对太阳光的有效应用。目前很多方法被用来提高TiO₂光催化效率, 如金属/非金属掺杂、贵金属负载、异质结构建和与碳材料复合等, 这些策略在提高光催化剂的光催化效率中, 涉及到如何兼顾太阳光利用和光生空穴和电子氧化还原能力两者之间的平衡。通常, 半导体禁带宽度越窄, 半导体的光谱响应范围越宽、太阳光利用越多, 但光生空穴和电子氧化还原能力越弱。因此, 想要提高TiO₂的光催化性能, 应考虑以下两个方面的平衡: 即降低带隙宽度, 拓展半导体的光谱响应范围; 与之同时使价带电位更正, 导带电位更负之间的平衡。然而, 这两个点是相互矛盾的, 因此很难在单组分光催化剂中同时实现这两点。

然而, Z型光催化剂可以同时满足这两点要求, 即: 降低半导体的带隙, 同时使导带更负, 价带更正, 因为Z光催化系统利用了两种半导体的优势, 其电荷转移机制类似于自然界中绿色植物的光合作用, 其中的载流子传输途径包括两步激发, 类似于英文字母“Z”, Z型光催化剂因此而得名。Z型光催化剂既能保留较高还原能力的光生电子和又能保留较高氧化能力的光生空穴, 由于Z型光催化剂特有的优点, 在光催化领域的应用越来越广泛。

本文综述了TiO₂基Z型光催化剂的最新研究进展, 其中包括: Z型光催化机理、应用范围和光催化活性改进方法。Z型光催化剂分为传统液相Z型光催化体系, 全固态Z型光催化体系, 以及最近几年发展起来的直接Z型光催化体系。它们的主要应用包括: 光催化分解水产氢、二氧化碳还原制备太阳燃料、有机污染物光催化降解。论文进一步讨论了提高TiO₂基Z型光催化性能的方法, 包括pH值调控、电子导体选择、助催化剂使用、掺杂改性、组织形貌控制、两种半导体质量比优化等。最后, 提出了TiO₂基Z型光催化剂今后面临的挑战和发展前景展望。

关键词: 二氧化钛; Z型光催化剂; 光解水; 还原二氧化碳; 污染物降解

收稿日期: 2017-10-18. 接受日期: 2017-10-31. 出版日期: 2017-12-05.

*通讯联系人. 电话: (027) 87871029; 传真: (027) 87879468; 电子信箱: jiaguoyu@yahoo.com

#通讯联系人. 电子信箱: keithho@eduhk.hk

基金来源: 国家自然科学基金(51602207, 21433007, 51320105001, 21573170); 武汉理工大学材料复合新技术国家重点实验室创新基金(2017-ZD-4, 2016-KF-17); 湖北省自然科学基金(2015CFA001).

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