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Review

Recent advances on Bi_2WO_6 -based photocatalysts for environmental and energy applications

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ABSTRACT

Bismuth tungstate (Bi_2WO_6) has become a research hotspot due to its potential in photocatalytic energy conversion and environmental purification. Nevertheless, the limited light absorption and fast recombination of photogenerated carriers hinder the further improvement of the photocatalytic performance of Bi_2WO_6 . Herein, we provide a systematic review for the recent advances on Bi_2WO_6 -based photocatalysts. It starts with the crystal structure, optical properties and photocatalytic fundamentals of Bi_2WO_6 . Then, we focus on the modification strategies of Bi_2WO_6 based on morphology control, atomic modulation and composite fabrication for diverse photocatalytic applications, such as organic synthesis, water splitting, CO_2 reduction, water treatment, air purification, bacterial inactivation, etc. Finally, some current challenges and future development prospects are proposed. We expect that this review can provide a useful reference and guidance for the development of efficient Bi_2WO_6 photocatalysts.

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1. Introduction

The rapid growth of modern industry promotes the development of global economy, accompanied by huge energy consumption and environmental pollution [1]. The effective utilization of natural resources to solve environmental and energy problems for economic sustainable development has become the focus of scientific researchers [2–6]. Semiconductor photocatalysis emerges with great potential for addressing the above two issues as it can convert low-density and unstable solar energy into high-density and steady chemical energy and produce reactive oxygen species for degrading pollutants in the air or water [7–9].

The origin of semiconductor photocatalysis can be traced back to 1972, when Fujishima *et al.* [10] reported that n-type

semiconductor TiO_2 electrode can decompose water to O_2 and H_2 under ultraviolet (UV) irradiation, which has attracted extensive attentions of scientists. Since then, semiconductor photocatalysis has made a series of breakthroughs in the fields of environment and energy. Over the past decades, some photocatalysts have shown high photocatalytic activity. However, many of them are only active under UV irradiation because of their wide band gap, such as TiO_2 and ZnO and so on [11–15]. Obviously, the narrow light response range of photocatalytic materials greatly limits the utilization of sunlight, as visible light accounts for 43% of the whole solar spectrum. In order to utilize solar energy as much as possible, many photocatalysts with visible light activity have been developed [16].

Many bismuth-based compounds have narrow band gap due to the hybridization of Bi 6s and O 2p orbitals at the va-

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Fig. 1. Number of publications for keyword “Bi₂WO₆ AND photocatalytic” (data obtained from Web of Science on November 10, 2020).

lence band (VB) maximum, which are thus exploited to be visible light responsive photocatalysts, such as Bi₂S₃, BiVO₄, Bi₂O₃, etc [17–26]. Among the bismuth-based photocatalysts driven by visible light, Bi₂WO₆, as a typical Aurivillius-phase material, has attracted much attention due to its unique layered structure, benign visible light photocatalytic activities, high thermal and photochemical stabilities, environmental friendliness and so on [27–30]. As early as 1999, Bi₂WO₆ photocatalyst prepared by conventional solid state reaction was reported for O₂ evolution [31]. Up to now, Bi₂WO₆ has been synthesized by various methods, such as sol-gel method, co-precipitation method, molten salt method, solvothermal method and hydrothermal process [32–37]. Based on the different synthetic methods, a large number of Bi₂WO₆-based photocatalytic materials with different properties have been studied in the environmental, energy and biological fields, including water splitting, CO₂ reduction, water treatment, air purification, inactivation of bacteria, selective organic synthesis and so on [27, 38–47]. Previously, Zhang *et al.* [47] reviewed the progress in selective organic synthesis and fuel production of Bi₂WO₆. Recently, Yi *et al.* [30] summed up the photocatalytic applications of Bi₂WO₆ in the field of environment. Besides, the photocatalytic applications of Bi₂WO₆ were also mentioned in a few chapters of some reviews [48–51]. However, the modification strategies of Bi₂WO₆ for diverse photocatalytic applications have not been reviewed in detail. In particular, the research on Bi₂WO₆ is undergoing rapid increase with each passing day (Fig. 1), and it is necessary to review the environmental and energy applications of Bi₂WO₆ based on the different modifica-

tion strategies for promoting the further development of Bi₂WO₆.

In this review, the crystal structure, optical properties and photocatalytic fundamentals of Bi₂WO₆ are first introduced. Then, we mainly review the modification strategies of materials to improve the photocatalytic performance of Bi₂WO₆, including morphology control, atomic modulation and composite fabrication. Meanwhile, recent advances on environmental, energy and related applications and the photocatalytic mechanism of Bi₂WO₆-based photocatalysts are also investigated. Finally, we discuss the current challenges and propose possible research directions in the future of Bi₂WO₆-based photocatalysts.

2. Crystal structure, optical properties and photocatalytic fundamentals of Bi₂WO₆

2.1. Fundamentals of photocatalysis

The principle about semiconductor photocatalysis is based on the energy band theory. The band structure of semiconductors is discontinuous, in which the top full band filled with valence electrons is called VB. In addition, the bottom empty band not occupied by valence electrons is called conduction band (CB), and the energy gap between CB and VB is forbidden band. The photocatalytic process of semiconductors is shown in Fig. 2(a) [7]. The photogenerated electron-hole pairs are generated from semiconductor when it absorbs photon with energy greater than or equal to its energy gap under light irradiation, and the photoexcited electrons transition from VB to CB, leaving relatively stable holes in VB. Photogenerated electrons and holes have strong reduction ability and oxidation ability, respectively. In the process of migration from the semiconductor interior to the surface, most of the electrons and holes will inevitably combine. Finally, the electrons and holes that reach the semiconductor's surface will react with various molecules adsorbed on the surface. In the process of pollutant degradation and bacterial disinfection, it is mainly achieved by the formation of superoxide radicals, hydroxyl radicals or other active groups. CO₂ reduction mainly depends on the reaction of photogenerated electrons with H₂O and CO₂. Water splitting is divided into two half reactions, in which photogenerated electrons react with H⁺ to release H₂, and photogenerated holes react with H₂O to produce O₂.

Photocatalytic reaction efficiency is closely related to the following factors: (1) the light absorption capacity of photo-

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Fig. 2. (a) Schematic illustration of semiconductor photocatalysis: (I) the formation of photogenerated carriers; (II) the recombination process of photogenerated carriers; (III) the reduction reaction of electrons (IV) the oxidation reaction of holes; (V) the further photocatalytic mineralization; (VI) the trapping of CB electrons at active sites on the surface of photocatalyst; (VII) the trapping of VB holes at the surface active sites of the photocatalyst. Adapted with permission from Ref. [7]. Copyright 2014, Royal Society of Chemistry. (b) Crystal structure of Bi₂WO₆. (c) Redox potentials of a variety of species and band energy positions of Bi₂WO₆ photocatalyst.

catalysts, including light absorption range and conversion efficiency; (2) the separation and transfer efficiencies of photogenerated electron-hole pairs; (3) catalytic reaction on the surface of photocatalysts [52,53]. Therefore, the photocatalytic performance is highly affected by the electronic structure and surface state of the semiconductors. In short, the photocatalysts need both narrow band gap and strong redox ability. The narrow energy gap is beneficial to the wide photo-response region. The strong redox ability of electrons and holes is more favorable for their respective reduction and oxidation reactions in thermodynamics. However, there is an essential contradiction between the above two aspects. Consequently, it is necessary to adopt proper modification strategies for various photocatalytic applications.

2.2. Structure and property characteristics of Bi₂WO₆ photocatalyst

Bi₂WO₆, as one of the simplest Aurivillius oxides, has an orthorhombic structure, which is composed of [Bi₂O₂]²⁺ layers linked with corner-shared [WO₄]²⁻ layers (Fig. 2(b)) [29,54,55]. The unique sandwiched structure of Bi₂WO₆ can induce built-in electric field between layers, which is beneficial to the separation of photogenerated electrons and holes. Density functional theory (DFT) calculations can be employed to study the contribution of orbitals to the VB and CB. It is generally accepted that VB of Bi₂WO₆ is predominated by the hybrid orbitals of Bi

6s and O 2p and CB of Bi₂WO₆ is formed by W 5d orbitals [56]. Based on this, the band gap of Bi₂WO₆ is generally between 2.6 and 2.9 eV depending on the position of VB and CB, which enables it to be a visible light responsive photocatalyst [44,57–61]. Generally speaking, the VB maximum and CB minimum represent the limit of oxidation potential of holes and reduction potential of electrons, respectively. Some thermodynamic data in the photocatalytic reaction process are shown in Fig. 2(c). It can be clearly seen that the CB and VB of Bi₂WO₆ can meet the requirements for degradation of most pollutants and energy conversion.

However, as a photocatalyst, Bi₂WO₆ has the following problems: (1) although it can absorb visible light, Bi₂WO₆ can only absorb visible light with wavelength less than 450 nm because of the limitation of band gap; (2) the recombination rate of photogenerated electrons and holes of Bi₂WO₆ is still high; (3) the exposed surface reactive sites on Bi₂WO₆ are not enough, which limit the adsorption and activation of reactants [62–64]. Therefore, optimizing the above properties of Bi₂WO₆ photocatalyst is the key to enhance its photocatalytic activity. The main modification methods include morphology control, atomic modulation and composite fabrication.

3. Morphology control

The performance of photocatalytic materials depends not only on their chemical composition, but also on their size and morphology. A high specific surface area with more active sites is conducive to enhancing the adsorption capacity of reactants. In addition, according to the equation $\tau = r^2/\pi^2D$ (τ , r , π and D stand for the average diffusion time of charge carriers from the interior to the surface, the particle size, a constant and the diffusion coefficient, respectively) [65,66], the photocatalysts with ultra-small or ultra-thin structures can reduce the charge diffusion path, thus effectively separating the photogenerated electrons and holes. In recent years, a variety of three-dimensional (3D), two-dimensional (2D), one-dimensional (1D) and zero-dimensional (0D) Bi₂WO₆ photocatalysts have been prepared to maximize their photocatalytic activity.

3.1. 3D structures

The 3D nano/microstructures, e.g. flower-like microstructure, always exhibit large specific surface area and abundant channels, which are beneficial to the adsorption of reactants. Besides, 3D structures can overcome the difficulty of recovery of nanocatalysts in liquid-phase reaction system. At present, researchers have prepared a large number of 3D Bi₂WO₆ nanostructures with various morphologies, which are mainly achieved by hydrothermal/solvothermal methods. By controlling reaction temperature, reaction time and pH value, and changing surfactant and template, flower-like [45], erythrocyte-like [32], single-crystal-like [35], and 3D hollow [67] structures can be obtained.

The hierarchical flower-like Bi₂WO₆ microspheres were prepared by hydrothermal process in acidic solution with the aid of L-lysine (Figs. 3(a) and (b)) [45], which converted tolu-

ene to benzaldehyde with a high selectivity under visible light irradiation. In contrast with Bi_2WO_6 with other morphologies (nanoparticles, nanoplates and nests), flower-like Bi_2WO_6 showed the highest benzaldehyde production rate ($464 \mu\text{mol/g/h}$), which was due to the multiple reflection of light on the Bi_2WO_6 microspheres. The authors also compared the oxidation of other aromatic alkanes and demonstrated that only the α -carbon of C–H bond was activated. Besides, it was revealed that holes were the most important oxidation species in the dehydrogenation of toluene, and O_2 participated in the formation of aldehyde groups. Similarly, Zhao *et al.* [68] prepared a series of Bi_2WO_6 with different morphologies by controlling the solvent, temperature and pH value (Fig. 3(c)). Among them, flower-like Bi_2WO_6 composed of nanoplates exhibited the highest photocatalytic performance for ceftriaxone sodium degradation, which may be attributed to the larger specific surface area and faster electron transfer process. However, there is still room for improvement in the photocatalytic activity of the hierarchical 3D Bi_2WO_6 .

In order to further improve the separation efficiency of photogenerated carriers, our group prepared 3D Bi_2WO_6 self-assembled by single-unit-cell layer with sodium dodecyl benzene sulfonate (SDBS) as surfactant (Figs. 3(d)–(f)) [69]. As shown in Fig. 3(g), Bi^{3+} ions first formed Bi-DBS complex by interacting with DBS^- ions, which prevented the hydrolysis of Bi^{3+} ions and promoted its dispersion in solution. After that, single-unit-cell layer Bi_2WO_6 nanosheets are formed by the reaction of Bi-DBS complex and WO_4^{2-} . Finally, Bi_2WO_6 nanosheets self-assembled into 3D hierarchical Bi_2WO_6 microspheres to minimize the surface energy. Compared with Bi_2WO_6 microspheres composed of nanosheets with thickness of ~ 20 nm, both the adsorption ability and photocatalytic deg-

radation efficiency of single-unit-cell layer (1.6 nm) 3D Bi_2WO_6 were greatly improved. Also, single-unit-cell layer Bi_2WO_6 exhibited a significantly enhanced photocatalytic H_2 evolution rate ($5.6 \mu\text{mol/g/h}$), which was 14 times higher than that of bulk Bi_2WO_6 (Fig. 3(h)). It indicated that single-unit-cell structure improved the oxidation and reduction properties of 3D Bi_2WO_6 , and the increased carrier density and separation efficiency were the main reason for the excellent photocatalytic performance of Bi_2WO_6 . These studies demonstrated that 3D flower-like Bi_2WO_6 microspheres have an excellent photocatalytic performance, and the photocatalytic performance can be further improved by optimizing the building unit of 3D structure.

In addition to these common photocatalytic behaviors, the hierarchical flower-like Bi_2WO_6 can also be used as micro-robots to actively move, gather, and target solid pollutants through oxidation pathways under light irradiation [70]. The movement mechanism of the self-propelled microrobots was shown in Fig. 4(a). Due to the non-uniform surface and exposure of Bi_2WO_6 , the active species produced by Bi_2WO_6 were unevenly distributed under the photocatalytic chemical reaction, thus forming a local electrolyte concentration around Bi_2WO_6 , which made them move autonomously through self-diffusion electrophoresis. Fig. 4(b) showed the trajectory of autonomous movement of some microrobots under light, and it was found that H_2O_2 can enhance the movement speed. The main active species (holes and hydroxyl radicals) produced by Bi_2WO_6 , benefited from the close contact between Bi_2WO_6 and textile surface, can rapidly decompose cellulose on textiles (Fig. 4(c)).

In addition to the typical flower-like Bi_2WO_6 microspheres, other 3D Bi_2WO_6 were also reported. Li *et al.* [32] prepared

Fig. 3. (a,b) Scanning electron microscope (SEM) images of flower-like Bi_2WO_6 microsphere. Adapted with permission from Ref. [45]. Copyright 2016, Royal Society of Chemistry. (c) SEM images of flower-like Bi_2WO_6 . Adapted with permission from Ref. [68]. Copyright 2018, Elsevier. (d,e) SEM images of single-unit-cell layer 3D Bi_2WO_6 . (f) Atomic force microscopy (AFM) images and corresponding height profiles (insets) of single-unit-cell layer 3D Bi_2WO_6 . (g) Formation diagram of single-unit-cell layer 3D Bi_2WO_6 . (h) Photocatalytic H_2 evolution over single-unit-cell layer 3D Bi_2WO_6 ($\lambda > 420$ nm). Adapted with permission from Ref. [69]. Copyright 2017, Elsevier.

Fig. 4. (a) Schematic illustration of motion mechanism of the Bi_2WO_6 microrobots. (b) Time-lapse images of the Bi_2WO_6 microrobots moving in water and H_2O_2 respectively under dark and visible light irradiation. (c) The clustering of Bi_2WO_6 microrobots under illumination and their further contact with textile fibers. Adapted with permission from Ref. [70]. Copyright 2020, Wiley-VCH.

erythrocyte-like 3D Bi_2WO_6 by anionic self-regulation strategy (Figs. 5(a) and (b)). Due to the existence of excessive WO_4^{2-} ions, the morphology of Bi_2WO_6 changed from microsphere to erythrocyte-like structure, and the rate constant k for photocatalytic degradation of Rhodamine B (RhB) was also improved by 1.62 times. The specific surface area and mesoporous were increased by this morphological transformation, which also enhanced the transfer and separation of carriers. Afterwards, a novel mesoporous Bi_2WO_6 tetragonal structure was realized by molten salt method for the first time [35]. The formation of single-crystal-like structure is attributed to the addition of alkali nitrates and electrostatic attraction within the crystal. The formation mechanism and morphology of the structure are shown in the Figs. 5(c)–(e). This unique structure allowed Bi_2WO_6 excellent photocatalytic activity for the degradation of organic dyes and O_2 production.

The construction of 3D hollow structure is also an important strategy to increase the specific surface area and simultaneously enhance light absorption. Jiang *et al.* [71] developed Bi_2WO_6 with a 3D hollow structure assembled by Bi_2WO_6 quantum dots (QDs) by solvothermal method (Fig. 6(a)). The hollow structure showed a large specific surface area, which greatly improved the CO_2 adsorption capacity of Bi_2WO_6 . More importantly, the hollow Bi_2WO_6 had a higher CB position, which enhanced the reduction ability of Bi_2WO_6 . In addition, a novel rod-shaped hollow 3D Bi_2WO_6 was successfully prepared using the hydrolysate of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$ as the precursor (Figs. 6(b) and (c)) [72]. The transition from solid rods to hollow structures can be explained by the Kirkendall effect. The details were as follows: Firstly, WO_4^{2-} ions exchanged with NO_3^- ions from the hydrolysis products of $\text{Bi}(\text{NO}_3)_3 \cdot 5\text{H}_2\text{O}$, resulting in the corrosion of the solid rod-like surface and the formation of porous structure. Then the Bi_2WO_6 crystal nuclei were formed on the surface as the growth sites, which made the internal ions

Fig. 5. (a,b) SEM images of erythrocyte-like Bi_2WO_6 and the photograph of erythrocyte (the insert of a). Adapted with permission from Ref. [32]. Copyright 2015, Elsevier. (c) Crystal growth process of Bi_2WO_6 . (d) Layered structure of Bi_2WO_6 . (e) SEM images of Bi_2WO_6 at the different reaction times. Adapted with permission from Ref. [35]. Copyright 2015, American Chemical Society.

Fig. 6. (a) SEM image of 3D hollow Bi_2WO_6 . Adapted with permission from Ref. [71]. Copyright 2017, Elsevier. (b,c) SEM images of Bi_2WO_6 hierarchical structures. (d) Schematic illustration of the Bi_2WO_6 evolution process. (e) N_2 adsorption-desorption isotherms. Adapted with permission from Ref. [72]. Copyright 2018, Elsevier.

gradually disappear and completely converted into Bi_2WO_6 (Fig. 6(d)). Compared with bulk Bi_2WO_6 , the specific surface area of hollow structures was increased by 58 times (Fig. 6(e)). In the absence of any sacrificial agent, it showed high photocatalytic activity of CO_2 reduction, which was 8 times that of bulk Bi_2WO_6 .

At present, a variety of 3D Bi_2WO_6 have been prepared to realize the excellent photocatalytic performance. However, it is difficult to achieve fine regulation in building units, porosity and active sites. Additionally, due to the limitation of reaction conditions, there is a lack of *in-situ* characterization technique of kinetics and structure in the synthetic process. It is expected that more efficient synthetic methods will be developed to construct 3D Bi_2WO_6 with better photocatalytic performance.

3.2. 2D structures

Compared with 3D nano/microstructure, the advantage of 2D nanostructure is that it has a shorter charge transport path, which is conducive to the separation of photogenerated electron-hole pairs. In addition, 2D materials also have many other excellent properties, such as large specific surface area, high adsorption to reactants and abundant active sites. Therefore, the preparation and research of 2D materials have attracted much attention from researchers.

Zhang *et al.* [73] firstly prepared Bi_2WO_6 nanoplates by hydrothermal method (Fig. 7(a)), which showed a high photocatalytic performance due to the large surface area. Since then, 2D Bi_2WO_6 materials have been developed continuously. For instance, the porous Bi_2WO_6 nanosheets were synthesized by hydrothermal method using cetyltrimethylammonium bromide (CTAB) as surfactant (Fig. 7(b)) [74]. The nanosheets with a thickness of 16 nm showed greatly improved photocatalytic performance for Cr(VI) reduction because of the porous structure and large specific surface area. Recently, Wu *et al.* [27] synthesized a special ultrathin Bi_2WO_6 with a thickness of two unit cells, the outermost layer of which is bilayer Bi_2O_3 (Figs. 7(c) and (d)). Due to this special outer surface, ultrathin Bi_2WO_6 exhibited an excellent photocatalytic performance for

Fig. 7. (a) SEM image of Bi₂WO₆ nanoplates. Adapted with permission from Ref. [73]. Copyright 2005, American Chemical Society. (b) SEM image of Bi₂WO₆ nanosheets. Adapted with permission from Ref. [74]. Copyright 2018, Elsevier. (c) The morphology of Bi₂WO₆. (d) The cross-section morphology of Bi₂WO₆. (e) Schematic diagram of photocatalytic reaction on Bi₂WO₆ surface and the energy positions of CB and VB for Bi₂WO₆-O, Bi₂WO₆-Cl and Bi₂WO₆-Br. Adapted with permission from Ref. [27]. Copyright 2020, American Chemical Society.

H₂ production under simulated sunlight irradiation. The photocatalytic activity was further enhanced by dye sensitization and Pt deposition. In addition, this structure can form Bi-Cl/Bi-Br bond by chemical adsorbing Cl⁻/Br⁻, thus reducing the recombination of photogenerated electrons and holes and decreasing the band gap (Fig. 7(e)).

For 2D materials, the synthesis of atomically-thin layer is considered as a favorable way to improve the photocatalytic performance. However, Bi₂WO₆ is connected by chemical bond between interlayer, and the bond energy is larger than that of van der Waals force. Therefore, it is difficult to realize single-unit-cell or even monolayer Bi₂WO₆. Fortunately, through the continuous exploration of researchers, the atomically-thin Bi₂WO₆ has successfully been prepared by hydrothermal method with the assistance of surfactant. Liang *et al.* [75] successfully prepared single-unit-cell Bi₂WO₆ with sodium oleate as surfactant for the first time (Fig. 8(a)). In the synthetic pro-

cess, oleic acid ions and Bi³⁺ ions formed lamella Bi-oleate complex, which played a very significant role in the synthesis of Bi₂WO₆. As a result, the methanol generation rate of single-unit-cell Bi₂WO₆ photocatalyst was 75 μmol/g/h, which was 125 times higher than that of bulk Bi₂WO₆. The huge photocatalytic performance improvement was owing to the high specific surface area and increased charge density on the surface (Figs. 8(b)–(f)). Furthermore, Zhou *et al.* [56] prepared monolayer Bi₂WO₆ with the assistance of CTAB. The monolayer Bi₂WO₆ had a sandwich structure of [BiO]⁺–[WO₄]^{2–}–[BiO]⁺, which allowed the photogenerated holes to directly generate in the surface layer and the photogenerated electrons to generate in the intermediate layer, thus achieving efficient charge separation (Figs. 8(g)–(i)). DFT calculation showed that the VB of Br⁻ modified monolayers shifted upward because Br 4*p* orbital was involved in the formation of VB. Compared with nanocrystalline Bi₂WO₆, monolayer Bi₂WO₆ exhibited an excellent H₂ evolution activity due to the large specific surface area and negative potential.

Unfortunately, even if the thickness of the 2D Bi₂WO₆ can be reduced to a single layer and the separation efficiency of photogenerated carriers is improved, there is still a high probability of recombination of photogenerated carriers due to the strong coulomb force. Cao *et al.* [76] reported an interesting work on photochromic Bi₂WO₆/amorphous BiOCl nanosheets for photocatalytic oxidation of toluene (Figs. 9(a) and (b)). The color of Bi₂WO₆/amorphous BiOCl changed from light yellow to blue under visible light irradiation, and can be recovered under atmospheric oxygen (Fig. 9(c)). In this process, the effect of BiOCl was negligible. X-ray photoelectron spectra (XPS), Raman spectra and synchrotron radiation X-ray absorption fine structure (XAFS) spectra revealed the generation of the [W(VI)O₆–x]

Fig. 8. (a) Transmission electron microscope (TEM) image. Density of states (DOS) of (b) single-unit-cell Bi₂WO₆ and (c) bulk Bi₂WO₆. Charge density distribution for the CB edge of (d) single-unit-cell Bi₂WO₆ and (e) bulk Bi₂WO₆. (f) Photocatalytic methanol evolution. Adapted with permission from Ref. [75]. Copyright 2015, Wiley-VCH. (g) TEM image and the corresponding HRTEM image of Bi₂WO₆. (h) AFM image of the monolayer Bi₂WO₆. (i) Schematic illustration of photocatalytic mechanism on the monolayer Bi₂WO₆. Adapted with permission from Ref. [56]. Copyright 2015, Springer Nature.

Fig. 9. (a) SEM image of the Bi_2WO_6 nanosheets and corresponding magnified image (inset). (b) TEM image and AFM image (inset) of the Bi_2WO_6 nanosheets. (c) Digital photographs and (d) XPS spectra of Bi_2WO_6 in the initial and coloured state. (e) Raman spectra for pristine Bi_2WO_6 and the p- Bi_2WO_6 sample series. (f) XAFS characterization for pristine Bi_2WO_6 and the p- Bi_2WO_6 sample series and magnification of the section indicated by a dashed box (inset). (g,h) Energy band scheme, microscopic structure and working mechanism of photocatalytic Bi_2WO_6 . Adapted with permission from Ref. [76]. Copyright 2018, Springer Nature.

site (Figs. 9(d)–(f)). In other words, the W–O–W bond was partially broken, accompanied by the generation of W=O bond, which shortened the W–O distance and weakened the peak intensity. The existence of $[\text{W}_{(\text{VI})}\text{O}_{6-x}]$ units continuously consumed the photogenerated electrons, which effectively inhibited the recombination of photogenerated carriers (Figs. 9(g) and (h)). Based on this, the as-prepared materials showed an excellent toluene conversion rate (97% within 24 h), far exceeding the known photocatalysts and even most of the thermal catalysts. In addition, it was found that the activation of C–H bond through photogenerated holes was a key step in the whole reaction process. This research provides us with a new effective strategy to improve the photocatalytic performance.

From the above, it can be seen that the surface state of 2D Bi_2WO_6 has a great influence on the photocatalytic performance. Especially in the gas-solid reaction process of CO_2 reduction, surface properties are particularly important. Liu *et al.* [77] modified the surface of Bi_2WO_6 nanosheets with different halogen atoms, which greatly improved the CO_2 reduction performance of Bi_2WO_6 . The CO productivity of Bi_2WO_6 modified by Br atoms was the highest, reaching $13.8 \mu\text{mol/g/h}$ (Fig.

10(a)). Experiments and theoretical calculations showed that surface halogenation can achieve adsorption and activation of CO_2 molecules and efficient separation of photogenerated charges. More importantly, through the calculation of the Gibbs free energy of the reaction process, the modification of Br atom reduced the formation energy of $^*\text{COOH}$ intermediate and accelerate the CO_2 conversion process (Fig. 10(b)). At present, CTAB has been widely used as surfactant to synthesize Bi_2WO_6 . However, some special and deep mechanism remains to be found. Liu *et al.* [78] studied the thin-layer structure of Bi_2WO_6 with hydrophobic and non-polar surface brought by CTAB. The non-polar modified hydrophobic surface promoted the mass transfer and adsorption of CO_2 and products CO, and inhibited the adsorption of H_2O . Therefore, it showed high efficiency of CO generation and further conversion of CO to CH_4 (Figs. 10(c) and (d)).

Currently, a variety of 2D Bi_2WO_6 materials have been greatly developed with excellent photocatalytic properties, and their thickness can be controlled at the atomic level. However, 2D Bi_2WO_6 still needs to be greatly improved in size control and atomic functionalization. In addition, it is a good way to

Fig. 10. (a) CO₂ reduction rate of X-Bi₂WO₆; (b) Relative Gibbs free energy diagrams of the whole path of CO₂ reduction to CO for Bi₂WO₆ and Br-Bi₂WO₆. Adapted with permission from Ref. [77]. Copyright 2020, Wiley-VCH. (c) Photocatalytic CO₂ reduction performance after irradiation for 5 h. (d) Analysis of photocatalytic products and hydrophobic-hydrophilic properties. Adapted with permission from Ref. [78]. Copyright 2020, Elsevier.

prepare 2D Bi₂WO₆ by *in-situ* conversion to overcome the interlayer chemical bond interaction.

3.3. 1D and 0D structures

Over the past few years, low dimensional (1D or 0D) nanomaterials have been widely used in the field of photocatalysis because of their unique optical and electronic properties [79–83]. 1D materials have the advantages of short diffusion path and easy strain relaxation, which are beneficial to the separation of photogenerated carriers. For 0D materials, the surface atoms account for a significant proportion, which makes the surface DOS greatly increase. In addition, various quantum effects (quantum size effect, quantum confinement effect, quantum tunneling effect, etc.) are very important for the research and application of 1D/0D materials [84–86].

Liu *et al.* [36] reported the preparation of 1D hierarchical Bi₂WO₆ hollow tubes using Bi₂O₃ rods as the precursor by solvothermal method (Figs. 11(a) and (b)), which exhibited high photocatalytic performance for degradation of RhB due to its rapid charge carrier diffusion rate. Electrospinning is a low-cost and high-efficiency technology for the preparation of 1D nanofibers, and the size of nanofibers can be well adjusted by controlling the precursors, solvents and technical parameters. For example, Yang *et al.* [87] successfully prepared Bi₂WO₆ nanofibers through electrospinning method (Fig. 11(c)), and the photocatalytic degradation efficiency of RhB reached 71% in 60 minutes. Unfortunately, the photocatalytic performance of Bi₂WO₆ nanofibers is lower than that of Bi₂WO₆ microspheres reported in this paper. At present, the research on 1D Bi₂WO₆ is still in its infancy, and more synthetic methods need to be developed. In addition, the photocatalytic performance of 1D Bi₂WO₆ is still not satisfactory, which is far below our expectation.

Fig. 11. (a,b) SEM images of the Bi₂WO₆. Adapted with permission from Ref. [36]. Copyright 2013, Royal Society of Chemistry. (c) SEM image of Bi₂WO₆ nanofibers. Adapted with permission from Ref. [87]. Copyright 2017, Elsevier. (d) TEM image and HRTEM image (inset) of Bi₂WO₆ nanoparticles. (e) The EPR spectra. (f) Relative HeLa cell viabilities under different treatments. (g) Positron emission tomography images of mice under different treatments (Day 21, I: saline; II: indocyanine green + laser; III: W₁₈O₄₉ + laser; IV: Bi₂WO₆ + laser). Tumor lesions are highlighted by white circles and right panels show the tumor images in cross section. Adapted with permission from Ref. [41]. Copyright 2018, American Chemical Society.

Because of the ultra-small size, 0D materials can be stably dispersed in solvents, providing conditions for biotherapy. Zhang *et al.* [41] synthesized ultrafine Bi₂WO₆ nanoparticles functionalized by carboxylic acid groups (Fig. 11(d)), which exhibited a multifunctional synergy, including enhanced computed tomography (CT) imaging, photothermal therapy (PTT) and oxygen-free photodynamic therapy (PDT). Electron paramagnetic resonance (EPR) showed that Bi₂WO₆ nanoparticles can oxidize water to hydroxyl radicals in the absence of O₂ under 808 nm laser irradiation (Fig. 11(e)). Antitumor experiments *in vitro* and *in vivo* proved that PTT and PDT had a synergistic effect, which greatly improved the killing effect of Bi₂WO₆ nanoparticles on tumor cells, and had no obvious side effects on mice (Figs. 11(f) and (g)). These results reveal the broad prospects of Bi₂WO₆ nanoparticles in the treatment of cancer through PTT and oxygen-free PDT. Furthermore, the complex of Bi₂WO₆ nanoparticles and platelet membranes were synthesized, which overcame the shortcomings of Bi₂WO₆ alone and realized long-term circulation in the blood and penetration into deep tumors [88]. The working principle of the hybrid for tumor treatment was shown in Fig. 12.

Currently, the research on 1D and 0D Bi₂WO₆ is still rare due to the difficulties in preparation, and the photocatalytic performance of 1D and 0D Bi₂WO₆ is not ideal. Thus, it is urgent to develop effective strategies to improve their photocatalytic activity. Furthermore, the introduction of piezoelectric field might be a promising application to enhance the photocatalytic activity of 1D Bi₂WO₆ because of its easy deformation under

Fig. 12. Working process of PM-Bi₂WO₆ nanoparticles. In radiotherapy, oxygen reactions with the broken end of DNA and damages cells, leading to a deteriorated hypoxia condition that is helpful to recruit MDSCs and inhibits the function of CTLs. In PTT/PDT/RT treatment, PM-Bi₂WO₆ nanoparticles can convert H₂O into hydroxyl radicals under light without O₂ consumption. Therefore, the tumor microenvironment is not conducive to the recruitment of MDSCs. At the same time, it is helpful for CTLs to respond to stress condition, so as to effectively against tumors. Adapted with permission from Ref. [88]. Copyright 2020, Wiley-VCH.

stress. OD Bi₂WO₆ can be more focused on the field of biological therapy because of its excellent water solubility and the possibility of targeting cancer cells.

The Bi₂WO₆ photocatalysts with different morphologies and diverse photocatalytic applications are summarized in Table 1. As mentioned above, the electronic structure and optical properties of Bi₂WO₆ can be well adjusted by morphology control so

as to be better applied in various fields of photocatalysis. Of course, it should also be recognized that the development of controllable synthetic methods for Bi₂WO₆ with different size and morphology is the basic step. It is necessary to carry out further modification on the basis of morphology control so as to achieve better practical application of photocatalysis.

4. Atomic modulation

The photocatalytic performance of Bi₂WO₆ is related to its intrinsic characteristics, including the migration and separation efficiencies of charge carriers, light absorption range and surface state, etc. However, the electronic structure and optical properties of pure Bi₂WO₆ may not fully meet the requirements of photocatalysis. Therefore, it is necessary to modify Bi₂WO₆ to further improve its photocatalytic performance. The atomic modulation of Bi₂WO₆ can well control its chemical composition, atomic arrangement, crystal and electronic structures, thus improving its photocatalytic activity.

4.1. Doping

The element doping and substitution of Bi₂WO₆ is one of the research hotspots. Doping external elements into Bi₂WO₆ crystal lattice can adjust the energy band structure of Bi₂WO₆ crystal, expand the light absorption range, and increase the separation efficiency of photogenerated carriers. Up to now, researchers have paid much attention to Bi₂WO₆ doping with

Table 1

A summary of Bi₂WO₆ with various morphologies for diverse photocatalytic applications.

Photocatalyst	Synthetic method	Reaction conditions (light resource, amount or concentration of photocatalyst and target, etc)	Photocatalytic activity	Ref.
3D				
Hollow structures of Bi ₂ WO ₆ QDs	Solvothermal method	UV-Vis light; 0.2 g; /	CH ₃ OH production: 7.5 μmol/g/h	[71]
Single-unit-cell layer Bi ₂ WO ₆ hierarchical architectures	SDBS-assisted hydrothermal process	λ > 420 nm; RhB degradation: 1.0 g/L; 0.01 mmol/L; H ₂ evolution: 50 mg; 20 mL CH ₃ OH and 3 wt% Pt (co-catalyst)	RhB degradation: 93.1% (1 h) H ₂ evolution: 5.6 μmol/g/h	[70]
Flower-like Bi ₂ WO ₆	Hydrothermal method	λ > 400 nm; 50 mg; 8 mmol	Toluene conversion: 464 μmol/g/h (1.5% conversion) (96% selectivity)	[45]
Hollow Bi ₂ WO ₆ microspheres	Ultrasonic spray pyrolysis method	Simulated sunlight irradiation; 0.3 g; 3 L/min	NO removal: 44.5% (60 min)	[67]
Tetragonal Bi ₂ WO ₆	Molten salt method	λ > 400 nm; RhB/phenol degradation: 0.5 g/L; 10 mg/L 0.1 mL H ₂ O ₂ ; O ₂ evolution: 0.1 g; 0.1 mol/L AgNO ₃ (electron sacrificial agent)	RhB degradation: 0.072 min ⁻¹ Phenol degradation: 0.0085 min ⁻¹ ; O ₂ evolution: 84.8 μmol/g/h	[35]
Erythrocyte-like Bi ₂ WO ₆	Hydrothermal method	λ > 400 nm; 0.5 g/L; 10 mg/L	RhB degradation: 0.212 min ⁻¹	[32]
Flower-like Bi ₂ WO ₆ microspheres	Hydrothermal method	λ > 400 nm; 1.0 g/L; 5 mg/L	RhB degradation: 91% (3 h)	[89]
Bi ₂ WO ₆ with quadrangular body rectangular column structure	PVP-assisted hydrothermal process	/; 0.2 g/L; 5 mg/L	Methyl orange (MO) degradation: 74.3% (3 h)	[90]
Hierarchical Bi ₂ WO ₆ nanoarchitectures	Solvothermal method	Visible light irradiation; 0.5 g/L; 0.01 mmol/L	RhB degradation: 0.020 min ⁻¹	[91]
Mesoporous nanoplate multi-directional assembled Bi ₂ WO ₆	Solvothermal method	λ > 420 nm; 0.5 g; 2 mg/L NO, O ₂ , and N ₂ balance (400 mL/min)	NO removal: almost 100% (2 min)	[37]
2D				
Monolayer Bi ₂ WO ₆	CTAB-assisted hydrothermal process	λ > 420 nm; RhB degradation: 0.25 g/L; 0.01 mmol/L; H ₂ evolution: 0.2 g/L; 0.4 g ethylenediaminetetraacetic acid (EDTA, sacrificial reagent) and 0.3 wt% Pt (co-catalyst)	RhB degradation: 98% (25 min) H ₂ evolution: 4.5 μmol/g (6 h)	[56]
Single-unit-cell Bi ₂ WO ₆	Sodium oleate-assisted hydrothermal process	AM1.5G; 1.43 g/L; 0.5 mL/min	CH ₃ OH evolution: 75 μmol/g/h	[75]

(To be continued)

Table 1 (continued)

Photocatalyst	Synthetic method	Reaction conditions (light resource, amount or concentration of photocatalyst and target, etc)	Photocatalytic activity	Ref.
Photochromic Bi ₂ WO ₆ nanosheets	OTAC-assisted hydrothermal process	$\lambda > 400$ nm; 50 mg; 1 mmol (acetonitrile as solvent)	Toluene conversion : 2162 $\mu\text{mol/g/h}$ Product: benzyl alcohol, benzaldehyde and benzoic acid	[76]
Bi ₂ WO ₆ nanosheets	CTAC-assisted hydrothermal process	Simulated sunlight irradiation; 20 mg; 0.4 g EDTA; 10 $\mu\text{mol/L}$ rhodamine and Pt	H ₂ evolution: 73.12 $\mu\text{mol/g/h}$	[27]
Bi ₂ WO ₆ nanosheets	Hydrothermal process with precursor	$\lambda > 400$ nm; /; 5 mL/min	CH ₄ evolution: 8.02 $\mu\text{mol/g}$ (8 h)	[92]
Ultra-thin Bi ₂ WO ₆ porous nanosheets	Hydrothermal process	$\lambda > 420$ nm; 1.2 g/L; 10 mg/L	Cr (VI) degradation: 97% (100 min)	[74]
Flake-Like Bi ₂ WO ₆	Hydrothermal process	$\lambda = 254$ nm; 1.0 g/L; 5 mg/L	RhB degradation: 100% (180 min)	[93]
Halogenation-modified Bi ₂ WO ₆ nanosheets	Hydrothermal process with different modifiers	/; 50 mg; 0.084 g NaHCO ₃ and 300 μL H ₂ SO ₄ (2 M)	CO evolution: 13.8 $\mu\text{mol/g/h}$	[77]
Atomically thin Bi ₂ WO ₆ nanosheets	CTAB-assisted hydrothermal process	AM 1.5; 30 mg; high purity CO ₂ gas	CO evolution: 7.1 $\mu\text{mol/g/h}$	[78]
1D Hierarchical Bi ₂ WO ₆ hollow tubes	Solvothermal method with precursor	Simulated sunlight irradiation; 0.5 g/L; 0.01 mmol/L	RhB degradation: 99% (90 min)	[36]
Bi ₂ WO ₆ nanofibers	Electrospinning process	Under light irradiation; 1 g/L; 10 mg/L	RhB degradation: 70% (60 min)	[87]
Bi ₂ WO ₆ nanofibers	Electrospinning process	$\lambda > 400$ nm; 1.5 g/L; 20 mg/L	Methylene blue (MB) degradation: 94.7% (200 min)	[94]
Mesoporous TiO ₂ /Bi ₂ WO ₆ hollow superstructure	Hydrothermal process	Simulated sunlight irradiation; 0.5 g/L; 0.01 mmol/L	RhB degradation: 96% (60 min)	[95]
Bi ₂ WO ₆ nanofibers	Electrospinning process	Simulated sunlight irradiation; 1.0 g/L; 0.02 mmol/L	RhB degradation: 75% (70 min)	[96]
WO ₃ /Bi ₂ WO ₆ nanorods	Solvothermal method	$\lambda > 400$ nm; 1.0 g/L; 10 mg/L	RhB degradation: ~100% (4 h)	[97]
Bi ₂ WO ₆ /RGO composite nanofibers	Electrospinning process	380 nm $< \lambda < 750$ nm; 0.1 g; 25 mL methyl alcohol and 75 mL water	H ₂ evolution: 5611 μmol (6 h)	[98]
0D Bi ₂ WO ₆ nanoparticles	Oil bath	808-nm laser; 200 mg/L; /	Relative HeLa cell viabilities: 13% (24 h)	[41]
platelet membrane/ Bi ₂ WO ₆ nanoparticle hybrids	Oil bath	X-ray irradiation; /; /	Tumor volume: ~30% of its original size	[88]

metal (Mo, Ce, Sm, Ba, Gd, etc) and nonmetal (F, Br, N, PO₄ group, CO₃ group, etc) elements [99–106].

Metal doping is an important doping method to improve the photocatalytic performance of materials, including transition metal doping, rare earth metal doping, co-doping and so on [107–117]. Etogo *et al.* [103] successfully prepared Mo doped Bi₂WO₆ with porous biscuit-like morphology and adjustable band gap (Fig. 13(a)). Mo doping led to the introduction of impurity level in Bi₂WO₆ and reduced the CB position. Meanwhile, the light absorption of the material was enhanced (Fig. 13(b)). The experimental results showed that Bi₂Mo_{0.21}W_{0.79}O₆ exhibited a higher O₂ evolution rate (147.2 $\mu\text{mol/g/h}$) than pure Bi₂WO₆ and Bi₂MoO₆. Differently, our group [99] reported Gd³⁺ doped Bi₂WO₆ by partially substituting Bi³⁺, which resulted in the increased band gap of Bi₂WO₆. Gd³⁺ had a half filled 4f orbit, which was very favorable for the capture and release of electrons because of the shallow electron trap effect, thus realizing the efficient separation of electron-hole pairs. It was worth noting that excessive Gd³⁺ doping accelerated the recombination of photogenerated electron-hole pairs. Furthermore, some lanthanides have up conversion effect, which can convert low-energy light into high-energy light through multiple absorption and energy transfer. For instance, Er³⁺ doped Bi₂WO₆ photocatalyst was synthesized by Zhang *et al.* [118], which had three new absorption bands due to the transition of ground state (Fig. 13(c)). Compared with the pure Bi₂WO₆, the Er³⁺

doped Bi₂WO₆ exhibited an enormously enhanced photocatalytic activity for phenol degradation under simulated sunlight irradiation (Fig. 13(d)).

Fig. 13. (a) SEM image of the Bi₂Mo_{0.21}W_{0.79}O₆ and O₂ evolution rates of different samples (all samples with 5 wt% deposited Co₃O₄) under visible light irradiation. (b) UV-Vis diffuse reflectance spectra (DRS) of different samples. Adapted with permission from Ref. [103]. Copyright 2016, Royal Society of Chemistry. (c) UV-Vis DRS of the as-prepared samples. (d) Degradation efficiency of phenol under simulated sunlight irradiation. Adapted with permission from Ref. [118]. Copyright 2010, Elsevier.

Fig. 14. (a) Hg⁰ removal efficiency of different samples under visible light irradiation. (b) Reusability of Bi₂WO₆-I in photocatalytic oxidation of Hg⁰. Adapted with permission from Ref. [120]. Copyright 2020, Elsevier. (c) Degradation curves of RhB in different samples under visible light irradiation. (d) Schematic diagrams of the photodegradation of F-Ce-Bi₂WO₆. Adapted with permission from Ref. [100]. Copyright 2014, American Chemical Society.

Similar to metal doping, nonmetal doping also shows a positive effect on improving the photocatalytic efficiency. Photocatalytic activity of N doped Bi₂WO₆ was explored by Hoang *et al.* [119] via a two-step microwave-assisted and hydrothermal process. The doping of N atoms with appropriate concentration (atomic ratio of N:Bi = 0.5%) achieved the lowest charge recombination rate and most improved photocatalytic degradation efficiency of RhB. In addition, I doped Bi₂WO₆ was also

successfully prepared by Zhang *et al.* [120]. It was found that the removal efficiency of elemental Hg of I doped Bi₂WO₆ (87.6%) was significantly higher than that of pure Bi₂WO₆ (9.1%), and it also had good chemical stability (Figs. 14(a) and (b)). This was due to the decrease of CB position and the acceleration of charge transfer. Meanwhile, it was found that superoxide radicals and holes were the main active species. In order to further improve the separation efficiency of photogenerated carriers, our group [100] also explored the coupling effect of metal and nonmetal co-doping for improving the photocatalytic performance. The results showed that Ce and F co-doping synergistically promoted the photocatalytic degradation performance, among which Ce³⁺/Ce⁴⁺ redox couple acted as an electron scavenger to enhance the separation and transfer of photogenerated electrons and holes (Figs. 14(c) and (d)).

Compared with simple element doping, ionic group doping can better adjust the band structure and optical absorption properties, thus largely improving the photocatalytic activities of semiconductor photocatalysts. Li *et al.* [106] reported PO₄ doped Bi₂WO₆ photocatalyst, which showed excellent photocatalytic performance in treating various pollutants, including reduction of Cr (VI) and degradation of RhB, phenol and antibiotics. With increasing the PO₄ doping concentration, the morphology of Bi₂WO₆ gradually transformed from 2D nanoplates to 3D microspheres, and the surface area was increased. Besides, the photoluminescence (PL) spectra, fluorescence decay curves and photoelectrochemical tests revealed that the PO₄ doped Bi₂WO₆ effectively separated the photogenerated carriers (Figs. 15(a)–(d)). The PO₄ doped Bi₂WO₆ atomic layers with oxygen vacancies were also studied to reveal the role of local atomic modulation [121]. Theoretical calculation and experi-

Fig. 15. (a) PL spectra and (b) fluorescence decay curves of different Bi₂WO₆ samples. (c) The photocurrent curves and (d) electrochemical impedance spectra of different Bi₂WO₆ samples. Adapted with permission from Ref. [106]. Copyright 2016, Elsevier. (e) UV-Vis DRS of Bi₂WO₆, PO₄-Bi₂WO₆ and Vo-PO₄-Bi₂WO₆ atomic layers. Calculated DOS of (f) Vo-PO₄-Bi₂WO₆ atomic layers, (g) PO₄-Bi₂WO₆ atomic layers, (h) Bi₂WO₆ atomic layers and (i) bulk Bi₂WO₆. Adapted with permission from Ref. [121]. Copyright 2017, Elsevier.

mental results showed that a new donor level was generated in PO_4 doped Bi_2WO_6 with oxygen vacancies with increased DOS, which reduced the band gap and improved the carrier separation and transfer efficiency (Figs. 15(e)–(i)). Thus, an improved photocatalytic performance for reducing CO_2 to methanol with an evolution rate of $157 \mu\text{mol/g/h}$ was obtained.

In short, doping is a simple and effective means to achieve atomic modulation, thus regulating the electronic structure of Bi_2WO_6 . However, it should also be noted that it is difficult to control the distribution of dopants, and there is little discussion on the internal mechanism between doping and morphology control.

4.2. Defect engineering

Crystal defects can adjust the electronic structures of materials and the interaction between atoms, such as bond energy, binding energy, electronegativity and charge density distribution, which can change the dielectric properties, optical properties and thermodynamic properties of materials [122–130]. Therefore, crystal defect engineering can improve the photoabsorption and dynamic process of charges, thus enhancing the photocatalytic activity. In this section, we pay attention to the role of vacancies in Bi_2WO_6 photocatalysts.

As a kind of crystal defects, oxygen vacancies have been widely studied in many catalysts due to their excellent properties: (1) the relatively low formation energy; (2) the enhance-

ment of photoresponse attributed to the introduction of defect state; (3) the improved separation efficiency of photogenerated carriers due to the role of electron capture and release by oxygen vacancies. Huo *et al.* [131] prepared Bi_2WO_6 with different concentrations of oxygen vacancies for photocatalytic oxidation of NO. The activation of O_2 molecules was a key step in the NO oxidation reaction, and the theoretical calculations showed that V2 was the most likely position of oxygen vacancy because of the lowest formation energy (Fig. 16(a)). The DOS indicated that Bi_2WO_6 with oxygen vacancies had a lower VB and CB edges than pure Bi_2WO_6 , implying that the oxidation ability of holes was enhanced (Figs. 16(b) and (c)). It can be seen from Figs. 16(d) and (g) that Bi_2WO_6 with oxygen vacancies weakened the O–O bond of adsorbed O_2 . In addition, the charge density and charge difference distribution suggested that O_2 adsorbed on the surface of Bi_2WO_6 with oxygen vacancies was easier to be activated (Figs. 16(e), (f), (h), and (i)). Based on these advantages of oxygen vacancies, NO oxidation reaction was promoted. Similarly, Kong *et al.* [132] synthesized UV-Vis-NIR-responsive Bi_2WO_6 with oxygen vacancies by using ethylene glycol as the solvent, which realized CO_2 reduction under broad solar spectrum because of its strong absorption in Vis-NIR region (Fig. 16(j)). In addition, Li *et al.* [43] introduced oxygen vacancies in Bi_2WO_6 nanosheets by Ar plasma treatment, which were confirmed by largely increased EPR signals (Fig. 16(k)). It was found that Bi_2WO_6 nanosheets with oxygen vacancies displayed a better photocatalytic performance for converting CO_2 to CO with a rate of $40.6 \mu\text{mol/g/h}$, which is due to the enhanced light absorption and increased separation efficiency of photogenerated carriers.

In addition to the widely studied oxygen vacancies, metal defect engineering is also a promising strategy to achieve efficient photocatalytic performance. Di *et al.* [133] fabricated single-unit-cell Bi_2WO_6 nanosheets with Bi vacancies using BiOBr nanosheets as templates by a hydrothermal ion-exchange method. The existence of Bi vacancies was revealed by the high-angle annular dark field scanning transmission electron microscope (HAADF-STEM) (Figs. 17(a) and (b)). DFT calculations showed that Bi vacancies can form defect level and increase the DOS at the VB maximum, and Bi vacancies also promoted the adsorption and activation of H_2O molecules. Therefore, single-unit-cell Bi_2WO_6 nanosheets with Bi vacancies exhibited an excellent O_2 evolution rate ($100.13 \mu\text{mol/g/h}$) with high stability (Fig. 17(c)). Likewise, Xie *et al.* [134] reported the preparation of Bi_2WO_6 with Bi vacancies, which realized the efficient separation of photogenerated carriers because of the generation of strongly protonated hydroxyl groups. Therefore, the photocatalytic activity for removing gaseous toluene was significantly improved, which was about 32 times that of pure Bi_2WO_6 . In addition, it was also found that the excessively high Bi vacancy concentration had a partial inhibition effect in the photocatalytic process. Different from the above-mentioned surface defects, Huang *et al.* [135] prepared single-unit-cell Bi_2WO_6 with stable subsurface W vacancies by optimizing the crystallization rate. DFT calculations demonstrated the formation of defect energy level, which made the electrons easier to be excited by low-energy photons. The experimental results

Fig. 16. (a) Crystal structure of Bi_2WO_6 , in which V1, V2 and V3 represent three different positions of oxygen vacancies. DOS of (b) pure Bi_2WO_6 and (c) Bi_2WO_6 -V2. Adsorption and activation of O_2 on the surface of (d) pure Bi_2WO_6 and (g) Bi_2WO_6 with oxygen vacancy. The charge density of (e) pure Bi_2WO_6 and (h) Bi_2WO_6 with oxygen vacancy, respectively. The charge difference distribution of (f) pure Bi_2WO_6 and (i) Bi_2WO_6 with oxygen vacancy, respectively. Adapted with permission from Ref. [131]. Copyright 2019, Elsevier. (The purple, gray and red spheres represent Bi, W and O atoms, respectively.) (j) UV-Vis DRS of different samples. Adapted with permission from Ref. [132]. Copyright 2016, Royal Society of Chemistry. (k) EPR spectra of Bi_2WO_6 and $\text{V}_0\text{-Bi}_2\text{WO}_6$. Adapted with permission from Ref. [43]. Copyright 2020, Royal Society of Chemistry.

Fig. 17. (a) Aberration-corrected HAADF-STEM images of the V_{Bi} -rich Bi_2WO_6 . (b) Clear structural model showing surface Bi vacancies in a. (purple balls represent atom and the blank represents the Bi vacancy on the surface in the model.) (c) Cycling curves of V_{Bi} -rich Bi_2WO_6 for O_2 evolution. Adapted with permission from Ref. [133]. Copyright 2018, Elsevier. (d) Schematic illustration of photocatalytic mechanism over the V_{W} - Bi_2WO_6 . Adapted with permission from Ref. [135]. Copyright 2019, American Chemical Society. (e) DOS of Bi_2WO_6 with or without double defect. Transient infrared absorption spectra of (f) Bi_2WO_6 with Bi–O vacancy pairs and (g) plate-structured Bi_2WO_6 . Adapted with permission from Ref. [29]. Copyright 2015, Wiley-VCH.

indicated that the photogenerated holes were the key reactive species for the oxidation of benzyl alcohol, and the photogenerated electrons were captured through W vacancies and finally reacted with O_2 (Fig. 17(d)). The single-unit-cell Bi_2WO_6 with W vacancies showed a significant improvement in the solar-driven catalytic efficiency for benzyl alcohol oxidation (55% in 8 h), which was 1.4 times and 3 times higher than that of single-unit-cell Bi_2WO_6 and bulk Bi_2WO_6 , respectively.

In addition, double defects engineering also shows a promising future. Zhang *et al.* [29] synthesized Bi_2WO_6 bipyramids with Bi–O vacancy pairs using PVP as surfactant via a solvothermal process. Theoretical calculations and the transient infrared absorption spectroscopy showed that the Bi–O vacancies on the high energy surface reduced the band gap and improved the separation efficiency of photogenerated carriers (Figs. 17(e)–(g)). As a result, the efficient photocatalytic degradation performance of diclofenac was realized under solar light irradiation.

As revealed by the existing research results, defect engineering is a promising method to improve the photocatalytic activity of Bi_2WO_6 . In fact, defects are more likely to be a double-edged sword, which have both advantages and disadvantages for the photocatalytic reaction process. In many cases, their disadvantages are rarely shown in the literatures. Therefore, it is a great challenge to overcome the shortcoming of defects and give full play to its advantages through reasonable design.

Obviously, atomic modulation is an effective mean to improve the photocatalytic performance of the pristine Bi_2WO_6 , which shows a broad prospect for photocatalytic applications. Table 2 summarizes the previous works on Bi_2WO_6 modified by atomic modulation for diverse photocatalytic applications. However, the accurate control on the position, concentration

and structure of atoms remains challenging. In addition, it is difficult to observe the state of atoms intuitively and synchronously by the current characterization technologies.

5. Composite fabrication

Although the photocatalytic activity of Bi_2WO_6 is greatly improved by morphology control and atomic modulation, the separation efficiency of photogenerated carriers is not satisfactory because there is only one component in the photocatalytic system and the charge recombination possibility is still high. Fabrication of composite photocatalysts is considered as one of the most popular and effective modification strategies to improve the utilization of solar energy and promote charge carriers separation [143–149]. At present, the materials for coupling Bi_2WO_6 mainly include metal-based materials, carbon-based materials and semiconductors.

In this section, the concept of cocatalyst is emphasized, as follows: It refers to the substances that have almost no catalytic effect but can tremendously enhance the catalytic activity of the photocatalysts, including metal materials and most carbon-based materials [150–152]. Even in semiconductor heterostructures, cocatalysts are added to enhance the interface properties. The close contact between the cocatalyst and the semiconductor leads to the strong interaction between them, which can significantly facilitate the transfer of photogenerated electron-hole pairs, adjust the band structure of the semiconductor, boost the light absorption capacity of the system, and then enhance the photocatalytic activity. Theoretically, this interaction can be regulated by the selection of cocatalyst, the control of size and morphology, and the interface state of contact.

Table 2A summary of Bi₂WO₆ modified by atomic modulation for diverse photocatalytic applications.

Photocatalyst	Reaction conditions (light resource, amount or concentration of photocatalyst and target)	Photocatalytic activity	Ref.
Doping	N doped Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 0.01 mmol/L	RhB degradation: 81% (30 min) [119]
	Gd doped Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 0.01 mmol/L	RhB degradation: 99% (2 h) [99]
	Ce and F co-doped Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 0.01 mmol/L	RhB degradation: ~100% (3 h) [100]
	PO ₄ doped Bi ₂ WO ₆	$\lambda > 400$ nm; 0.5 g/L; 10 mg/L (0.05 g citric acid)	Cr (VI) reduction: 0.159 min ⁻¹ [106]
	Mo doped Bi ₂ WO ₆	$\lambda > 420$ nm; 100 mg; 0.02 mol/L Na ₂ S ₂ O ₈ and 0.1 mol/L NaOH and (samples with 5 wt% deposited Co ₃ O ₄)	O ₂ evolution: 147.2 μ mol/g/h [103]
	PO ₄ doped V ₀ -Bi ₂ WO ₆	AM1.5 G; /; CO ₂ gas	CH ₃ OH evolution: 157 μ mol/g/h [121]
	Lu doped Bi ₂ WO ₆	/; 1.0 g/L; 0.1 mmol/L	RhB degradation: ~92% (3 h) [136]
	Yb doped V ₀ -Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; /	RhB degradation: 95% (3 h) [137]
	La doped Bi ₂ WO ₆ ; Ce doped Bi ₂ WO ₆ ; Gd doped Bi ₂ WO ₆ ; Yb doped Bi ₂ WO ₆	Simulated solar irradiation; /; 10 mg/L	RhB degradation: ~100% (120 min); ~100% (120 min); ~100% (90 min); ~100% (90 min); [138]
	Cu doped Bi ₂ WO ₆	LED lamp (460 nm); 2.0 g/L; 15 mg/L	Norfloxacin degradation: 90% (60 min); [139]
	Mg doped Bi ₂ WO ₆ ; Fe doped Bi ₂ WO ₆ ; Zn doped Bi ₂ WO ₆ ; Cu doped Bi ₂ WO ₆ ; Fe doped Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 10 mg/L	Ciprofloxacin degradation: 0.0267 min ⁻¹ ; 0.0446 min ⁻¹ ; 0.0570 min ⁻¹ ; 0.0460 min ⁻¹ ; [140]
		$\lambda > 420$ nm; 20 mg; 10 mmol toluene	Benzaldehyde formation rate: 1303.8 μ mol/g/h (selectivity: 96.8%) [141]
Defect engineering	V _W -Bi ₂ WO ₆	Simulated sunlight irradiation; 5 g/L; 0.2 mol/L (trifluorotoluene saturated with O ₂ as solvent)	Benzyl alcohol conversion: 55% (8 h) (> 99% selectivity) Product: benzaldehyde [135]
	V _{Bi} -Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 0.05 mol/L AgNO ₃ (electron sacrificial agent)	O ₂ evolution: 100.13 μ mol/g/h [133]
	V _{Bi} -Bi ₂ WO ₆	420 nm < λ < 780 nm; 0.1 g; 25 mg/L	Toluene removal: ~100% (3 h) [134]
	V ₀ -Bi ₂ WO ₆	$\lambda > 420$ nm; 0.2 g/L; /	NO removal: 47% (30 min) [131]
	V _{Bi-O} -Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 20 mg/L	Diclofenac degradation: 3.127 h ⁻¹ [29]
	V _W -Bi ₂ WO ₆	$\lambda > 420$ nm; 20 mg; 0.01 mol/L	Phenol degradation: 80% (6 h) [142]
	V ₀ -Bi ₂ WO ₆	Simulated solar light; /; CO ₂ and water vapour (5 mL/min)	CH ₄ evolution: 13.9 μ mol/g (8 h) [132]
	V ₀ -Bi ₂ WO ₆	/; 10 mg; high-purity CO ₂	CO evolution: 40.6 μ mol/g/h [43]

5.1. Metal-based composites

As the most commonly used type of cocatalyst, metals, especially noble metals, exhibit many excellent optical, electronic and chemical properties. Therefore, coupling with metals is deemed to be a superior mean to advance the photocatalytic performance of semiconductors. There are two main features for metal-semiconductor composite photocatalysts: Schottky barrier and local surface plasmon resonance (LSPR). When a n-type semiconductor (such as Bi₂WO₆) is modified by noble metal particles, the surface electrons of semiconductor will transfer to the metal because of the higher work function of the metal compared with the semiconductor (Fig. 18(a)) [7]. Therefore, Schottky barrier formed on the interface can effectively improve the charge separation efficiency. LSPR refers to that the metal nanoparticles can absorb photons with the same frequency as the unique resonance frequency of metals, thus achieving strong electron oscillations (Fig. 18(b)) [153]. Generally speaking, there are three possible mechanisms for LSPR effect: (1) local heating that increases the generation amount of excitons from semiconductors; (2) near-field enhancement that promotes the transfer of photons to semiconductors; (3) hot electron injection that enhances carrier concentration of semiconductors (Figs. 18(c)–(e)) [154,155]. These processes are likely to occur simultaneously in metal-based composites, making it difficult to distinguish the respective contribution of

each effect.

Hu *et al.* [156] successfully assembled Au nanorods on Bi₂WO₆ nanosheets with the assistance of mercaptopropionic

Fig. 18. (a) Schematic of the Schottky barrier. Adapted with permission from Ref. [7]. Copyright 2014, Royal Society of Chemistry. (b) The dynamic process of metal nanoparticles during irradiation (i.e., LSPR). Adapted with permission from Ref. [153]. Copyright 2020, American Chemical Society. LSPR-related mechanisms, including (c) local heating, (d) near-field enhancement and (e) hot electron injection. Adapted with permission from Ref. [155]. Copyright 2018, Royal Society of Chemistry.

acid. The Au cocatalyst loaded on Bi_2WO_6 forming Schottky barrier allowed the electrons to transfer from the CB of Bi_2WO_6 to the Au nanorods, realizing the effective charge separation. The Au nanorods also had a wide range of light absorption. As a result, Au modification enhanced the photocatalytic activity of Bi_2WO_6 nanosheets driven by near infrared light, and the efficiency of MO degradation reached 71% in two hours. In addition, Au modified Bi_2WO_6 on titanium substrate also had an excellent antibacterial property [157]. The results showed that the LSPR realized the charge transfer from Au towards Bi_2WO_6 , which led to the appearance of more reactive oxygen species and stronger photothermal effect (Figs. 19(a) and (b)). Accordingly, the Au modified Bi_2WO_6 composite coating demonstrated an antibacterial rate of 99.87% and 99.93% against *Escherichia coli* and *Staphylococcus aureus*, respectively, after irradiation by 808 nm near infrared light for 15 min. Furthermore, Wang *et al.* [158] discussed the effect of deposition of dual-metals on Bi_2WO_6 nanosheets. Because the electrons transferred from Bi_2WO_6 to Au and finally to Pd, the carrier separation was realized more effectively. As a result, the metal codeposition strategy improved the selective oxidation activity of benzyl alcohol.

In addition to noble metal, Bi metal can also be applied as cocatalyst to enlarge the light absorption and charge separation efficiency of semiconductors. The cost of Bi is also lower than that of noble metals, such as Au, Pt, Ag, etc. Therefore, Bi-based composites have brought widespread attention because of its excellent properties. Zhang *et al.* [159] prepared Bi modified Bi_2WO_6 ($\text{Bi}/\text{Bi}_2\text{WO}_6$) composites by employing ethylene glycol

as reducing agent. The experimental results exhibited that the NO removal efficiency of $\text{Bi}/\text{Bi}_2\text{WO}_6$ composite reached 53.1%, which was much higher than that of Bi metal (7.7%) and pure Bi_2WO_6 (8.6%). The reason for the performance improvement was that the LSPR effect of Bi improved the separation efficiency of carriers, which resulted in the formation of more active species (Figs. 19(c) and (d)). Besides metal deposition, Bi-modified Bi_2WO_6 can also be obtained by self-reduction of Bi_2WO_6 . The advantage of this method is the intimate interface between the metal and Bi_2WO_6 , which also enhances the stability of the composites. Our group demonstrated that Bi decorated Bi_2WO_6 photocatalysts were prepared by *in-situ* reduction method using NaBH_4 as the reducing agent [160], and the reduction degree of Bi_2WO_6 can be well adjusted by changing the concentration of NaBH_4 (Fig. 19(e)). It was found that the Bi modified Bi_2WO_6 with $\text{NaBH}_4/\text{Bi}_2\text{WO}_6$ molar ratio of 0.2 had the greatest photocatalytic performance for phenol degradation, which was 3 times than that of Bi_2WO_6 (Fig. 19(f)). The enhanced photocatalytic activity was attributed to the improvement of light absorption and the LSPR effect of Bi metal.

Although metal-based Bi_2WO_6 composites have made good progress in the field of photocatalysis, the mechanism of charge transfer between metal and Bi_2WO_6 still needs to be further understood, and the in-depth mechanism of LSPR effect of metals should also be proved by advanced characterization techniques. In addition, the relationship among the morphology, size and distribution of metals and the photocatalytic performance of metal- Bi_2WO_6 composite photocatalysts should be further elucidated.

5.2. Carbon-based composites

As a kind of cost-effective cocatalyst, carbon materials with conjugated π structure have high electrical conductivity and special electronic properties, which can be used as excellent electron acceptor and donor to reduce the recombination of photogenerated electrons and holes, significantly improving the photocatalytic performance of semiconductors [161–165]. At present, many carbon materials have been applied for photocatalysis, including amorphous carbon, graphene, fullerene, conducting polymers, graphitic carbon nitride ($\text{g-C}_3\text{N}_4$) and so on [166–168]. Among them, $\text{g-C}_3\text{N}_4$ as a semiconductor material is discussed in the following section.

Wang *et al.* [39] prepared Bi_2WO_6 nanoparticles supported on porous carbon framework by hydrothermal method. Benefiting from the increased charge separation efficiency and light absorption, the 5 wt% carbon/ Bi_2WO_6 composite had the best photocatalytic activity for RhB degradation, which was 2.1 times that of pure Bi_2WO_6 . Besides, N modified biochar was also demonstrated to be a carrier for improving the photocatalytic activity of Bi_2WO_6 because of its special layered structure and excellent conductivity [169]. Carbon quantum dots (CQDs) have attracted much attention due to its biocompatibility, non-toxicity, easy synthesis and other excellent properties. Qian *et al.* [170] synthesized CQDs modified Bi_2WO_6 photocatalysts through a self-assembly route. CQDs/ Bi_2WO_6 composites exhibited a red shift of light absorption edge and im-

Fig. 19. (a) Photothermal heating curves. (b) Photocatalytic mechanism of the Au modified Bi_2WO_6 composite. Adapted with permission from Ref. [157]. Copyright 2019, Elsevier. EPR signals of (c) the DMPO•OH and (d) DMPO• $\text{O}_2\cdot^-$ adducts in the dark and under visible irradiation. Adapted with permission from Ref. [159]. Copyright 2019, Elsevier. (e) UV-Vis DRS of pure Bi_2WO_6 and $\text{Bi}_2\text{WO}_6\text{-X}$. (f) Photocatalytic degradation curves and apparent rate constants. Adapted with permission from Ref. [160]. Copyright 2017, Elsevier.

proved photocurrent response (Fig. 20(a)), thus achieving high photocatalytic activity for oxidizing acetone to CO_2 , which was about 2 times that of pure Bi_2WO_6 (Fig. 20(b)). For the sake of revealing the interfacial interaction between CQDs and Bi_2WO_6 , CQDs/ Bi_2WO_6 nanocomposites were synthesized by hydrothermal method [171]. DFT calculations showed that high charge density was produced at the interface of the composite, and the electrons were enriched in the CQDs region, while the holes were accumulated in the Bi_2WO_6 region, realizing efficient spatial separation of charges (Figs. 20(c)–(e)). Moreover, CQDs also had up conversion effect, which can absorb the full solar spectrum. Therefore, the CQDs/ Bi_2WO_6 composite performed enhanced photocatalytic performance for the degradation of MO and bisphenol A (BPA) under visible and infrared light irradiation.

Graphene is always used for constructing composite photocatalysts because it has a huge specific surface area, fast carrier mobility, outstanding chemical stability and other remarkable physical and chemical properties derived from its unique sp^2 hybrid orbit [172–174]. Dong *et al.* [175] synthesized reduced graphene oxide (RGO)/hollow spherical Bi_2WO_6 composites by a simple hydrothermal reaction. The results showed that 1 wt% RGO/ Bi_2WO_6 had the best photocatalytic performance for the degradation of several organic wastewater, including RhB, MO, phenol, sulfamonomethoxine and sulfanilamide. The enhanced photocatalytic performance of the composite was attributed to the enhancement of light absorption and charge separation efficiency. However, when the content of RGO was higher than 1 wt%, the photocatalytic performance decreased, which may be on account of the fact that the excess RGO hindered the light absorption of Bi_2WO_6 and acted as the recombination center of electrons and holes. In addition, Dong *et al.* [176] also successfully prepared Bi_2WO_6 /graphene aerogel composites, which not only had the advantages of graphene composites, but also showed improved the adsorption ability of

pollutants and good recovery capacity, existing a high practical significance for wastewater purification.

Conducting polymers with large conjugated π system is a kind of new materials developed in recent decades, which can be applied in photocatalysis because of their high conductivity. Dai *et al.* [168] prepared Bi_2WO_6 hollow microspheres and used different conductive polymers (polyaniline, polypyrrole and polythiophene) for decoration. Polythiophene modified Bi_2WO_6 had the best photocatalytic performance for CO_2 reduction. The yields of methanol and ethanol are 56.5 $\mu\text{mol/g/h}$ and 20.5 $\mu\text{mol/g/h}$ in 4 h, respectively, and the total yield was 2.8 times that of pure Bi_2WO_6 . The improved CO_2 reduction activity benefited from the narrow energy gap and high charge mobility of polythiophene. Mxenes materials have emerged as a new star in the field of materials since their discovery in 2011, and some achievements have been made in the field of photocatalysis [177,178]. Cao *et al.* [179] fabricated ultrathin $\text{Ti}_3\text{C}_2/\text{Bi}_2\text{WO}_6$ nanosheets, which showed significantly improved photocatalytic performance of CO_2 reduction with the irradiation of simulated solar light. It was attributed to that Ti_3C_2 promoted electron movement, increased the specific surface area and promoted the adsorption of CO_2 (Fig. 21). In addition, Ti_3C_2 also had special photothermal conversion characteristics, which can activate Bi_2WO_6 photocatalyst.

The carbon materials always show excellent conductivity and have a variety of sources with relatively low cost, so they are promising to be used for improving the photocatalytic activity of Bi_2WO_6 . At present, graphene was the most often applied for fabricating composite photocatalysts, but the researches on Mxenes and conductive polymers are relatively scarce. The development of Mxenes or polymers Bi_2WO_6 composite photocatalysts with high photocatalytic activity is a promising direction.

5.3. Semiconductor heterojunction

The construction of semiconductor heterojunctions is an effective way to enlarge the photoresponse range and carrier separation efficiency of photocatalysts [180–187]. Semiconductor heterojunction photocatalysts are composed of two or

Fig. 20. (a) The photocurrent density of pristine Bi_2WO_6 and CQDs/ Bi_2WO_6 under visible ($\lambda > 420$ nm) light irradiation. (b) CO_2 formation rate in photocatalytic oxidation of acetone under visible light irradiation. Adapted with permission from Ref. [170]. Copyright 2016, Elsevier. The side view of the spatial distributions of partial charge densities of the (c) VB maximum and (d) CB minimum states for CQDs/ Bi_2WO_6 . (e) Deformation charge density for CQDs/ Bi_2WO_6 . Adapted with permission from Ref. [171]. Copyright 2018, Elsevier.

Fig. 21. (a) Schematic band energy diagram of $\text{Ti}_3\text{C}_2/\text{Bi}_2\text{WO}_6$. (b) Transfer process of photogenerated electrons at the interface of $\text{Ti}_3\text{C}_2/\text{Bi}_2\text{WO}_6$. Adapted with permission from Ref. [179]. Copyright 2018, Wiley-VCH.

more semiconductors with different energy band structures through tightly connected interfaces. In general, traditional semiconductor heterojunction possesses three types: type I, type II and type III [7,8]. As displayed in Fig. 22, the type I junction owned a nested band structure, in which the CB position of semiconductor A is higher than the other, but its VB energy level is lower than that of semiconductor B. Therefore, the electrons and holes generated by light excitation will migrate and gather towards the semiconductor with a smaller band gap, which reduces the redox potentials of photocatalyst and cannot achieve the purpose of charge separation. The type II junction has a staggered band structure, in which the CB and VB energy levels of one semiconductor are higher than those of the other one. The electrons and holes will migrate along opposite directions to achieve spatial separation. The type III junction has an un-intersected band structure, which makes it impossible for carriers to migrate between semiconductors. So far, the research on traditional heterojunction mainly concentrates on type II junction.

g-C₃N₄, as a carbon-based semiconductor material, has shown admirable potential in photocatalysis on account of its excellent chemical stability, nontoxicity, facile synthesis and appropriate band structure [188,189]. Wang *et al.* [46] fabricated core-shell structured g-C₃N₄@Bi₂WO₆ at low temperature. This structure was beneficial to charge separation between interfaces, which enables the photogenerated electrons easily to be injected into Bi₂WO₆ from g-C₃N₄, while photogenerated holes of Bi₂WO₆ were transferred to g-C₃N₄. As a result, more active species were produced and the degradation efficiency of phenol was greatly improved. The *in-situ* ion exchange method is a good strategy to achieve the close contact between Bi₂WO₆ and other semiconductors, so as to strengthen the photocatalytic activity. For instance, 2D Bi₂WO₆@Bi₂S₃ core-shell structure was successfully synthesized by an anion exchange process [190]. The emergence of Bi₂S₃ largely expanded the light response range (Fig. 23(a)). The photocatalytic efficiency for degradation of brilliant red X3B was increased to 16.5 times that of pure Bi₂WO₆. In addition, formation of homogeneous junction is also an interesting and effective method to enhance the photocatalytic performance of Bi₂WO₆. Xu *et al.* [191] first synthesized Bi₂WO₆ quantum dots and 2D Bi₂WO₆ by hydrothermal method, and then combined them by

Fig. 22. Schematic illustration of the three different types of semiconductor heterojunction photocatalysts.

a simple self-assembly route. Due to the different morphologies, the positions of CB and VB of Bi₂WO₆ quantum dots and 2D Bi₂WO₆ were slightly distinct, thus forming a type II heterostructure (Fig. 23(b)), which was conducive to separate the charge carriers for improved degradation of 4-chlorophenol and RhB. Combining the advantages of plasma metals and heterojunction is a significant strategy to ulteriorly optimize the photocatalytic activity. For example, Dong's research group prepared Bi/Bi₂O₃/Bi₂WO₆ ternary composites via *in-situ* chemical reduction method using NaBH₄ as the reducing agent [192]. As shown in Fig. 23(c), the molar ratio of Bi, Bi₂O₃ and Bi₂WO₆ were adjusted by NaBH₄. In this system, the excited electrons transferred from Bi to Bi₂O₃ and finally to Bi₂WO₆. Unlike photoinduced electrons, the generated holes migrated directly from Bi₂WO₆ to the surface of Bi₂O₃, and then reacted with hydroxyl groups or water molecules to form hydroxyl radicals (Fig. 23(d)). Benefiting from the synergistic effect of heterojunction and LSPR, the removal efficiency of NO in this system reached 55.4%, which was much higher than that of pure Bi₂WO₆ (10%).

Semiconductor p-n junction is a special heterostructure composed of p-type and n-type semiconductors, which can achieve efficient charge separation [193,194]. A novel 2D/2D Bi₂WO₆/BiOI composite with p-n junction and surface oxygen vacancies was synthesized by Kong *et al.* [195]. The mechanism of this p-n junction was shown in Figs. 23(e) and (f). The Fermi

Fig. 23. (a) UV - Vis DRS of the different samples. Adapted with permission from Ref. [190]. Copyright 2018, Elsevier. (b) Schematic diagram of photocatalytic reaction mechanism. Adapted with permission from Ref. [191]. Copyright 2018, Elsevier. (c) The X-dependent phase conversion in the series of Bi₂WO₆ samples. (d) Schematic diagram of the possible reaction mechanism of Bi/Bi₂WO₆/Bi₂O₃ under visible light irradiation. Adapted with permission from Ref. [192]. Copyright 2018, Elsevier. (e) Band positions of BOI and Bi₂WO₆-OV. (f) The process of charge transfer and separation of p-n heterojunction for photocatalytic CO₂ reduction. Adapted with permission from Ref. [195]. Copyright 2019, Elsevier.

level (E_f) of Bi_2WO_6 (n-type semiconductor) is much higher than that of BiOI (p-type semiconductor). Therefore, when they contact each other, electrons diffuse from Bi_2WO_6 to BiOI , and holes diffuse from BiOI to Bi_2WO_6 . Finally, the energy band of BiOI moves up along with its E_f , while that of Bi_2WO_6 moves downward until the E_f of the system reaches equilibrium, thus forming an interfacial electric field from Bi_2WO_6 to BiOI . Under visible light irradiation, Bi_2WO_6 and BiOI are excited to form photogenerated electrons and holes. Due to the internal electric field, the holes in Bi_2WO_6 transfer to BiOI rapidly, while the transfer path of the electrons is opposite. Finally, the reasonable p-n heterostructure makes the photogenerated carriers achieve ultrafast directional migration and spatial separation. In addition, the surface oxygen vacancies of Bi_2WO_6 can capture electrons as the active center of CO_2 reduction. Due to these advantages, the composite achieved an excellent photocatalytic performance for CO_2 reduction under visible light irradiation, and the CH_4 yield reached $18.32 \mu\text{mol/g}$ in 8 h. Similarly, Xiang *et al.* [28] also synthesized $\text{Bi}_2\text{WO}_6/\text{BiOI}$ heterostructures by a straightforward hydrothermal method. The construction of p-n junction prolonged the lifetime of photogenerated carriers, allowing good antibacterial properties.

The traditional type II semiconductor heterojunction holds the ability of nicely enhance the separation efficiency of photogenerated carriers, but the directional migration of photogenerated electrons to more positive CB and holes to more negative VB will reduce the redox potentials of the original photogenerated electrons and holes. In addition, because of the electrostatic repulsion between the same kind of charges, it is difficult to migrate and enrich electrons and holes. For overcoming the shortcomings of type II junction, Z-scheme that is similar to plant photosynthesis has attracted intense attentions [196–200]. In comparison with the traditional type II semiconductor heterojunction, Z-scheme junction can not only achieve efficient charge separation, but also retain the inherent redox abilities of photocatalyst. As shown in Fig. 24, the development history of Z-scheme photocatalysts has gone through three generations, including liquid-phase Z-scheme, all-solid-state Z-scheme and direct Z-scheme junctions [201].

In the early Z-scheme photocatalytic system, the PS I and PS II has no direct contact, and the electron migration was realized through the electron acceptor/donor (A/D) pair. However, this system has some disadvantages. The electron A/D pair in PS-A/D-PS system is able to react with the photogenerated electrons in CB of PS I and the holes in VB of PS II, which will inevitably reduce the effective carrier number. In addition, the traditional Z-scheme system can only be constructed in the

liquid phase, which restricts their photocatalytic applications. Therefore, all-solid-state Z scheme is proposed to overcome these shortcomings, in which electron A/D pair is replaced by electron mediator, which greatly improves the ability of electron migration and prevents the shielding effect of electron A/D pair. Electronic mediators are generally played by materials with good conductive properties, i.e., metals (Au, Ag, Ni, etc.) and conductive carbon-based materials (graphene, carbon nanotubes, CQDs, etc.) [202]. A $\text{Bi}_2\text{WO}_6/\text{RGO}/\text{C}_3\text{N}_4$ heterojunction was successfully fabricated by the hydrothermal method with two steps, and the synthesis scheme was shown in Fig. 25(a) [203]. It was found that the CB and VB positions of Bi_2WO_6 were separately +0.20 and +3.02 eV, severally, and that of C_3N_4 were –1.30 and +1.35 eV, respectively. The VB potential of C_3N_4 was lower than the standard oxidation potential of $\text{OH}^\bullet/\text{OH}$ (+2.4 eV vs. NHE), which was not consistent with the results of terephthalic acid PL probing experiment, so the traditional type II heterojunction theory was not suitable for this photocatalytic system. As a consequence, the more likely path of electron transfer was from CB of Bi_2WO_6 to VB of C_3N_4 through RGO and it combined with holes in VB of C_3N_4 . Finally, the holes were accumulated in the VB of Bi_2WO_6 and electrons were gathered in the CB of C_3N_4 , realizing efficient separation of photogenerated carriers. The main functions of RGO cocatalyst included acting as redox medium to improve Z-scheme charge transfer between C_3N_4 and Bi_2WO_6 and carrier to capture electrons from C_3N_4 (Fig. 25(b)). Under visible light irradiation, the all-solid-state Z-scheme system exhibited excellent photocatalytic reduction performance for conversion of CO_2 and H_2O to fuels (Fig. 25(c)).

In addition to using metal and carbon-based materials as conductors, ohmic contact may also be formed between two semiconductors, which is conducive to the realization of Z-scheme charge transfer without electronic mediators, so it is named as direct Z-scheme [201,202]. Compared with the type II heterojunction, the delocalized electrons in the CB of PS II in Z-scheme system will shuttle to the VB of PS I, which is thanks to the strong electrostatic attraction at the interface. Therefore, the photoexcited electrons and holes will be accumulated at the highest CB and the lowest VB of the Z-scheme system, rendering the strongest redox ability. Based on these favorable conditions, various direct Z-scheme systems have been developed on account of their excellent potential in the area of photocatalysis [204–206]. For example, a direct Z-scheme photocatalyst $\text{FAPbBr}_3/\text{Bi}_2\text{WO}_6$ without redox medium was prepared by Huang *et al.* [44] Ultrafast time-resolved infrared transient absorption spectroscopy was used to straightforward detect the charge transfer pathway. The infrared decay and rising curve (Figs. 25(d) and (g)) under 470 nm excitation revealed that the charge transfer path of heterojunction followed the transfer mechanism of type II heterojunction, while the transfer path of the charge followed the Z-scheme mechanism with 360 nm excitation (Figs. 25(e), (f), (h) and (i)). Under simulated sunlight, $\text{FAPbBr}_3/\text{Bi}_2\text{WO}_6$ Z-scheme photocatalyst realized the coupling of CO_2 reduction to CO ($170 \mu\text{mol/g/h}$) and benzyl alcohol oxidation to benzaldehyde ($250 \mu\text{mol/g/h}$). Recently, Jiang *et al.* [207] fabricated the direct Z-scheme CsP-

Fig. 24. Schematic illustration of liquid-phase Z-scheme system, all-solid-state Z-scheme system and direct Z-scheme system.

Fig. 25. (a) UV-Vis DRS of the different samples. (b) Schematic diagram of the reaction mechanism. (c) The photocatalytic CO, CH₄, H₂, and O₂ production rates. Adapted with permission from Ref. [203]. Copyright 2018, Elsevier. Ultrafast time-resolved infrared transient absorption spectroscopy of different sample (normalized optical density; OD). (d) Decay and (g) rising phase signals upon 470 nm excitation. (e) Decay and (h) rising phase signals upon 360 nm excitation. Transient changes over (f) microseconds and (i) milliseconds upon 360 nm excitation. The insets in d, e, f and i represent the electron interactions in their respective process. Adapted with permission from Ref. [44]. Copyright 2020, American Chemical Society.

bBr₃/Bi₂WO₆ heterojunction by electrostatic self-assembly (Figs. 26(a) and (b)). The construction of 2D/2D heterostructures was conducive to the formation of large-area heterogeneous interface and shortened the charge transfer distance of Z-scheme. The surface potential distribution was studied by photoassisted Kelvin probe force microscopy (Figs. 26(c)–(f)). The results showed that the surface potential difference between Bi₂WO₆ and CsPbBr₃ increased from 14.4 to 27.2 mV after illumination, which was attributed to collection of surface

photogenerated electrons of CsPbBr₃, thus verifying the charge transfer mechanism of Z-scheme in the system.

Composite fabrication combines the advantages of different materials and achieves efficient charge separation among different components. So far, Bi₂WO₆-based heterojunctions have been widely researched in environmental purification and energy generation (Table 3). Among them, the fabrication of Z-scheme junction shows the largest potential in the practical applications of Bi₂WO₆, which may attract the most interests.

Fig. 26. (a) Element mapping of CsPbBr₃/Bi₂WO₆. (b) AFM height image of selected area. (c) Surface potential images in the dark. (d) Surface potential images under light. (e) The corresponding line profiles of surface potential. (f) Schematic diagram of the charge transfer mechanism on CsPbBr₃/Bi₂WO₆. Adapted with permission from Ref. [207]. Copyright 2020, Wiley-VCH.

6. Conclusions and outlook

In this review, we summarize the recent progress of Bi₂WO₆-based photocatalysts in fields of energy and environment. Firstly, the basic properties and photocatalytic fundamentals of Bi₂WO₆ photocatalyst are briefly outlined. Then, some regulating strategies of Bi₂WO₆ materials are reviewed in

detail, including morphology control, atomic modulation and composite fabrication. Through these strategies, the light absorption and the separation efficiency of photogenerated electrons and holes can be significantly enhanced, and the surface properties can also be regulated, thus greatly strengthening the photocatalytic performance of Bi₂WO₆.

However, there are still many problems and challenges in the research of Bi₂WO₆ photocatalyst, and many existing limitations need to be broken in the future research work to make full use of the advantages of Bi₂WO₆ in the field of energy conversion and environmental purification:

(1) Though Bi₂WO₆ with various dimensions can be prepared by different synthetic methods, the large-scale, accurate and controllable synthesis of uniform Bi₂WO₆ is still a huge challenge. Particularly, the design of highly active facet, porous structure and QDs shows more promising prospect.

(2) Atomic modulation can effectively change the inherent characteristics of Bi₂WO₆, and then regulate its photocatalytic performance. However, it is still difficult to accurately control the atomic sites. At the same time, the photocatalytic process on the atomic sites needs to be further revealed by using advanced technical means. Secondly, surface grafting may be also an effective and urgently needed mean to achieve atomic control of Bi₂WO₆.

(3) Although composite fabrication has been widely used in

Table 3

A summary of fabrication of Bi₂WO₆-based composite for diverse photocatalytic applications.

Photocatalyst	Reaction conditions (light resource, amount or concentration of photocatalyst and target)	Photocatalytic activity	Ref.
Metal-based composites	Au-Pd-Bi ₂ WO ₆	Simulated sunlight irradiation; 2.5 g/L; 0.025 mol/L (acetonitrile as solvent)	Benzyl alcohol conversion: ~1.63 mmol/h/g (5 h) (72% selectivity); Bhenethyl alcohol conversion: ~1.0 mmol/h/g (5 h) (75% selectivity); 4-methoxy benzyl alcohol conversion: ~1.17 mmol/h/g (5 h) (62% selectivity) Product: the corresponding aromatic aldehyde [158]
	Pt-Bi ₂ WO ₆ with oxygen vacancy	$\lambda > 420$ nm; 30 mg; 250 mg/L	Gaseous toluene removal: 2.927 h ⁻¹ [208]
	Bi-Bi ₂ WO ₆	$\lambda > 400$ nm; 300 mg; 1.0 L/min	NO removal: 53.1% (30 min) [159]
	Au-Bi ₂ WO ₆	Visible light irradiation; 1.0 g/L; 20 mg/L	MO degradation: ~92% (120 min) [156]
	Bi-Bi ₂ WO ₆	$\lambda > 400$ nm; 1.0 g/L; 10 mg/L	RhB degradation: 92% (25 min) [209]
	Pt-Bi ₂ WO ₆	Simulated sunlight irradiation; /; 130 mL	4-methoxy benzyl alcohol conversion: 95% (4 h) (99% selectivity) Product: 4-methoxy benzaldehyde [210]
	Au-Bi ₂ WO ₆	$\lambda > 420$ nm; /; 20 mg/L	Ofloxacin degradation: 95% (3 h) [211]
	Bi-Bi ₂ WO _{6-x}	120 μ W/cm ² ; 0.25 g/L; 20 mg/L	BPA degradation: 0.55 h ⁻¹ [212]
	Ag-Bi ₂ WO ₆	/; 1.0 g/L; 0.01 mmol/L	RhB degradation: 0.033 min ⁻¹ [213]
	Ag-Bi ₂ WO ₆	simulated sunlight irradiation; 2.0 g/L; 0.01 mol/L	RhB degradation: 0.158 min ⁻¹ [214]
Carbon-based composites	Bi ₂ WO ₆ /Graphene Hydrogel	$\lambda > 420$ nm; 100 mg; 0.01mmol/L (static system)	MB degradation: ~50% (12 h) [215]
	CQDs/Bi ₂ WO ₆	$\lambda > 700$ nm; /; 5 mL/min	CH ₄ production: 0.41 μ mol/g (8 h) [216]
	N-Biochar/Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 10 mg/L	RhB degradation: 99.1% (45 min) [169]
			Cr(VI) reduction: 96.7% (30 min)
	CQDs/Bi ₂ WO ₆	$\lambda > 420$ nm; 20 mg; acetone gas	CO ₂ production: 380 mg/L [170]
	Graphene oxide/Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 10 mg/L	RhB degradation: ~93% (120 min) [217]
	Ti ₃ C ₂ /Bi ₂ WO ₆	Simulated sunlight irradiation; 0.1 g; 0.084 g NaHCO ₃ and 0.3 mL H ₂ SO ₄ (2 mol/L)	CH ₄ production: 1.78 μ mol/g/h [179]
			CH ₃ OH production: 0.44 μ mol/g/h
	Biomass carbon/Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 20 mg/L	Tetracycline hydrochloride (TC) degradation: ~85% (90 min) [218]
	Ti ₃ C ₂ /Bi ₂ WO ₆	$\lambda > 400$ nm; 20 mg; 5 μ L HCHO	CO ₂ product: 72.8 μ mol/g/h [219]
	N134 carbon black/Bi ₂ WO ₆	/; 1.0 g/L; 40 mg/L	TC degradation: 0.018 min ⁻¹ [220]

(To be continued)

Table 3 (continued)

Photocatalyst	Reaction conditions (light resource, amount or concentration of photocatalyst and target)	Photocatalytic activity	Ref.
Type II junction	Bi ₂ WO ₆ QDs/Bi ₂ WO ₆	$\lambda > 400$ nm; 1.0 g/L; /	RhB degradation: 0.32 min ⁻¹ [191]
	g-C ₃ N ₄ /Bi ₂ WO ₆	$\lambda > 420$ nm; 25 mg; 5 mg/L	4-Chlorophenol (4-CP) degradation: 0.65 min ⁻¹ [46]
	Carbon QDs/Bi ₂ WO ₆	Visible light irradiation; 1.0 g/L; 10 mg/L	Phenol degradation: ~0.075 h ⁻¹ [171]
	g-C ₃ N ₄ /Bi ₂ WO ₆	$\lambda > 420$ nm; 0.2 g/L; 1.25 mmol/L	MO degradation: 94.1% (1h)
	N doped g-C ₃ N ₄ /Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 10 mg/L	BPA degradation: 99.5% (2h)
	CdWO ₄ /Bi ₂ WO ₆	$\lambda > 420$ nm; 50 mg; 0.05 mmol (acetonitrile as solvent)	Ibuprofen degradation: ~96.1% (1h)
	P-La ₂ Ti ₂ O ₇ /Bi ₂ WO ₆	$\lambda > 420$ nm; 1.0 g/L; 10 mg/L	Phenol degradation: 93.1% (5 h)
	N doped TiO ₂ @Bi ₂ WO ₆	$\lambda > 400$ nm; 0.3 g/L; 40 mg/L	Benzene conversion: 7.3% (4 h)
	Monomeric hemin/Bi ₂ WO ₆	Simulated sunlight irradiation; 0.2 g/L; 10 mg/L	Product: phenol [222]
	Perylene diimide/Bi ₂ WO ₆	$\lambda > 420$ nm; 0.5 g/L; 5 mg/L	RhB degradation: ~99.02% (80 min)
	CuInS ₂ /Bi ₂ WO ₆	$\lambda > 420$ nm; 0.2 g; 5 μ L	TC degradation: 99.4% (90 min)
	NaYF ₄ : Yb ³⁺ , Gd ³⁺ , Tm ³⁺ @Bi ₂ WO ₆	Simulated sunlight irradiation; 0.25 g/L; 20 mg/L	TC degradation: 86.4% (1 h)
	Bi ₂ WO ₆ @Bi ₂ S ₃	$\lambda > 420$ nm; 1.0 g/L; 0.1 mmol/L	Phenol degradation: ~68% (3 h)
	Bi/Bi ₂ O ₃ /Bi ₂ WO ₆	$\lambda > 420$ nm; 0.2 g; 2.4 L/min	Toluene removal: 63% (5 h)
	Bi ₂ S ₃ /Bi ₂ WO ₆	AM 1.5G; 1.0 g/L; 20 mg/L	BPA degradation: 94% (180 min)
	BiPO ₄ /Bi ₂ WO ₆	Simulated sunlight irradiation; 0.5 g/L; 0.01 mmol/L	Brilliant red X-3B degradation: ~55% (90 min)
	Au decorated Bi ₂ WO ₆ /TiO ₂	420 nm < λ < 780 nm; 0.25 g/L; 20 mg/L	NO removal: 55.4% (30 min)
	MoS ₂ /Bi ₂ WO ₆	Visible light irradiation; 1.0 g/L; 10 mg/L	Ofloxacin degradation: 87% (3 h)
	Bi ₂ WO ₆ /RGO	Natural sunlight; /; 60 mg/L	MB degradation: 0.0305 min ⁻¹
	Ag ⁺ -CDs-Bi ₂ WO ₆	Simulated sunlight irradiation; 0.5 g/L; 20 mg/L	4-Nitroaniline conversion: ~100% (16 min)
	g-C ₃ N ₄ @Bi ₂ WO ₆	$\lambda > 400$ nm; 1.0 g/L; 20 mg/L	Product: 4-phenylenediamine
p-n junction	V ₀ -Bi ₂ WO ₆ /BiOI	$\lambda > 400$ nm; /; 50 mL/min	RhB degradation: 100% (50 min)
	Bi ₂ WO ₆ /BiOI	$\lambda > 420$ nm; 10 mg; /	RhB degradation: 95% (4 h)
	Co ₃ O ₄ /Bi ₂ WO ₆	Visible light irradiation; /; /	TC degradation: 92% (10 min)
	Bi ₂ WO ₆ /Bi ₂ S ₃ /MoS ₂	$\lambda > 420$ nm; 20 mg; 40 mg/L	2,4-Dichlorophenol degradation (2,4-DCP): 70% (3 h)
Z-scheme junction	Black phosphorus/Bi ₂ WO ₆	Visible light irradiation; NO removal: 80 mg; 10 mg/L (flow rate: 1.2 L/min) H ₂ evolution: 0.2 g/L; 10 mL triethanolamine (hole sacrificial agent) and 3 wt% Pt	CH ₄ production: 18.32 μ mol/g (8 h)
	Bi ₂ WO ₆ /CuBi ₂ O ₄	$\lambda > 400$ nm; 0.5 g/L; 15 mg/L	<i>P. aeruginosa</i> mortality: 100% (60 min)
	CuInS ₂ /Bi ₂ WO ₆	$\lambda > 420$ nm; 0.3 g/L; 10 mg/L	<i>P. aeruginosa</i> mortality: 100% (60 min)
	Bi ₂ WO ₆ /RGO/g-C ₃ N ₄	$\lambda > 420$ nm; 50 mg; /	Ciprofloxacin degradation: 86% (5 min)
	CsPbBr ₃ /Bi ₂ WO ₆	$\lambda > 420$ nm; 5 mg; high-purity CO ₂ gas (5 mL EA)	Cr(VI) reduction: 0.0361 min ⁻¹
	FAPbBr ₃ /Bi ₂ WO ₆	AM 1.5G; 10 mg; 0.1 mmol benzyl alcohol and CO ₂ gas (trifluorotoluene as solvent)	NO removal: 67% (30 min)
	AgBr/Bi ₂ WO ₆	$\lambda > 400$ nm; 1.0 g/L; /	H ₂ evolution: 4208.4 μ mol/g/h
	Bi ₂ WO ₆ /graphene QDs/WO ₃	Visible light irradiation; 0.2 g/L; 20 mg/L	NO removal: ~94% (60 min)
	Ag decorated WO ₃ /Bi ₂ WO ₆	Simulated sunlight irradiation; 0.2 g; 2 μ L	Tetracycline hydrochloride (TC) degradation: 92.4% (2 h)
	Bi ₂ Fe ₄ O ₉ /Bi ₂ WO ₆	$\lambda > 420$ nm; 0.3 g/L; 10 mg/L	CO production: 15.96 μ mol/g/h
			CH ₄ production: 2.51 μ mol/g/h
			O ₂ production: ~10.5 μ mol/g/h
			CH ₄ production: ~2.2 μ mol/g/h
			CO and CH ₄ production: 50.3 μ mol/g/h
			CO production: 170 μ mol/g/h benzyl alcohol conversion: 250 μ mol/g/h product: benzaldehyde
			TC degradation: 87.5% (60 min)
			Phenol degradation: 99.8% (120 min)
			Chlorobenzene removal: 80% (10 h)
			RhB degradation: ~100% (90 min)

the area of photocatalysis and has made great achievements, there are still many controversies about the transfer mechanism of photogenerated carriers at the interface. Therefore, *in-situ* characterization techniques need to be developed to observe the interfacial charge dynamics of photocatalysts. Moreover, composite fabrication can be coupled with atomic modulation to further enhance the photocatalytic performance, and the development of novel Bi₂WO₆-based composite system is also a good research topic.

(4) As a ferroelectric material, the photocatalytic performance of Bi₂WO₆ can be enhanced by coupling external fields, such as mechanical stress and temperature gradient [244–248]. In addition, the external electric field can also enhance the photocatalytic activity of Bi₂WO₆. However, the researches concentrating on the above-mentioned aspects are very few. The introduction of external field is expected to be a research hotspot in the future.

(5) The application of Bi₂WO₆ in environmental field is

mainly focused on the degradation of single pollutant in water. However, the pollutants are often complex in practical application, which leads to many difficulties to be overcome. Remarkably, Bi_2WO_6 has a very good application prospect in cancer treatment and antibacterial aspect. Besides, the efficiency for solar fuel production of Bi_2WO_6 still needs to be improved, and some new applications, such as nitrogen fixation, are worth exploring.

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Graphical Abstract

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Recent advances on Bi_2WO_6 -based photocatalysts for environmental and energy applications

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This review provides a systematic summary on the recent advances of Bi_2WO_6 -based photocatalysts in fields of energy and environment. More importantly, different modification strategies for improving the photocatalytic activity of Bi_2WO_6 were discussed.

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Bi₂WO₆基光催化剂在环境和能源领域的最新研究进展

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摘要: 随着全球经济的快速发展与人口的日益膨胀, 随之而来的能源消耗与环境污染也日益成为一个严峻的挑战。半导体光催化技术能够将低密度的太阳能转化为高密度的化学能, 此外它能够通过产生活性自由基来降解空气或水中的污染物, 因此在解决上述问题中具有巨大潜力, 被认为是有着广阔前景的绿色无污染的能源转化和环境修复手段。在过去几十年的研究中, 一些光催化剂表现出了较好的光催化活性, 如TiO₂和ZnO等。然而, 由于它们的宽带隙, 仅仅在紫外光下具有活性, 这极大地限制了其对太阳光的利用。为了尽可能地利用太阳能, 研究者们开发了许多具有可见光活性的光催化剂。

钨酸铋(Bi₂WO₆)作为一种典型的Aurivillius层状钙钛矿材料, 因具有独特的层状结构、良好的可见光催化活性、高的热稳定性和光化学稳定性及环境友好性等特点而备受关注。然而, 有限的光吸收和光生载流子的快速复合阻碍了Bi₂WO₆光催化性能的进一步提高。因此, 研究者们进行了大量的研究, 致力于进一步增强Bi₂WO₆光催化剂的活性。本文对Bi₂WO₆基光催化剂的最新研究进展进行了系统综述。首先介绍了Bi₂WO₆的晶体结构、光学性质和光催化基本原理。然后, 基于Bi₂WO₆的改性策略, 包括形貌控制、原子调控和复合材料制备, 重点讨论了Bi₂WO₆在水分解、污染物处理、空气净化、杀菌消毒、二氧化碳还原、选择性有机合成等领域的光催化应用。最后, 对Bi₂WO₆基光催化剂当前面临的挑战和未来的发展作了展望和总结, 提出了Bi₂WO₆光催化剂未来的一些研究方向, 包括(1)大规模、精确可控地合成Bi₂WO₆, 特别是高活性晶面、多孔结构和量子点的设计; (2)精确调控原子位置, 利用先进的技术手段进一步揭示活性位点上的光催化过程; (3)发展原位表征技术来观察复合光催化剂的界面电荷动力学以及开发新型Bi₂WO₆基复合体系; (4)通过机械应力、温度梯度以及电场等外场的耦合提高Bi₂WO₆的光催化性能; (5)进一步深入研究Bi₂WO₆在不同领域的光催化应用, 特别是在肿瘤治疗和太阳能燃料制备方面, 一些新的应用如固氮等也值得探索。期望本综述能够为Bi₂WO₆和其他高效光催化材料的设计提供一些指导和帮助。

关键词: Bi₂WO₆; 光催化剂; 形貌控制; 原子调控; 复合物制备

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