Proceedings of CONF-MCEE 2026 Symposium: Advances in Sustainable Aviation and Aerospace Vehicle Automation
DOI: 10.54254/2755-2721/2026.KA27955

Review of the Structure and Modification Methods of Bismuth-based Photocatalysts

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Abstract. With the development of human society, water environmental problems are becoming increasingly serious. The presence of various pollutants such as antibiotics, dyes, and pesticides in these wastewaters has had serious negative impacts on the environment and human health. The problems caused by the excessive discharge of various antibiotics have gradually attracted attention. Photocatalysis, as a green, pollution-free, and sustainable treatment technology, has stood out among a number of advanced oxidation technologies. Among various photocatalysts, bismuth-based photocatalysts, as a new material, have attracted much attention and been widely studied due to their visible light response characteristics, unique layered structure, and adjustable electronic band structure. However, their practical applications are also limited by issues such as band gap and photogenerated carrier recombination rate. This article reviews the basic principles and technological developments of photocatalysis. Taking Bi_2MoO_6 and BiOCl as examples, the principles of various modification methods for bismuth-based photocatalysts are discussed in detail, and the mechanisms by which different modification methods improve the photocatalytic effect are analyzed. This provides new ideas for the development of bismuth-based photocatalysts.

Keywords: Photocatalysis, Bismuth-based, heterojunction, antibiotics

1. Introduction

With the rapid development of the economy, water pollution issues are becoming more and more worthy of attention. In the process of development, the world produces about 1,000 km^3 of man-made wastewater each year, of which nearly 30% is urban wastewater and more than 60% is industrial wastewater. The various pollutants such as antibiotics, dyes, pesticides, etc. in these wastewaters have caused serious negative impacts on the environment and human health. Traditional wastewater treatment methods such as activated carbon adsorption and biodegradation have more or less limitations such as high cost, low efficiency, and incomplete degradation. Antibiotics, as a class of antimicrobial drugs with complex molecular compound structures, can destroy or reduce the activity of bacteria. According to data from Scaria [1] et al., global antibiotic consumption increased rapidly from 21 billion doses per day to about 35 billion doses between 2000 and 2015, an increase of almost 65%. In addition, Klein [2] et al. predicted that the use rate of antimicrobial drugs will continue to grow to 200% by 2030. Excessive use of antibiotics can lead to the emergence and

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DOI: 10.54254/2755-2721/2026.KA27955

spread of antibiotic resistance genes (ARGs), causing damage to human intestinal microorganisms, and ultimately having a negative impact on human health.

Nowadays, advanced oxidation technologies (AOPs) are widely studied, such as electrochemical oxidation, sonochemical oxidation, ozone oxidation, sulfate oxidation, photocatalytic oxidation, and Fenton oxidation. Photocatalytic technology is a research hotspot in the field of solar energy conversion and environmental purification. In recent years, significant progress has been made in the research of photocatalytic technology in the fields of water decomposition, hydrogenation, wastewater treatment, air purification, and coupled power generation.

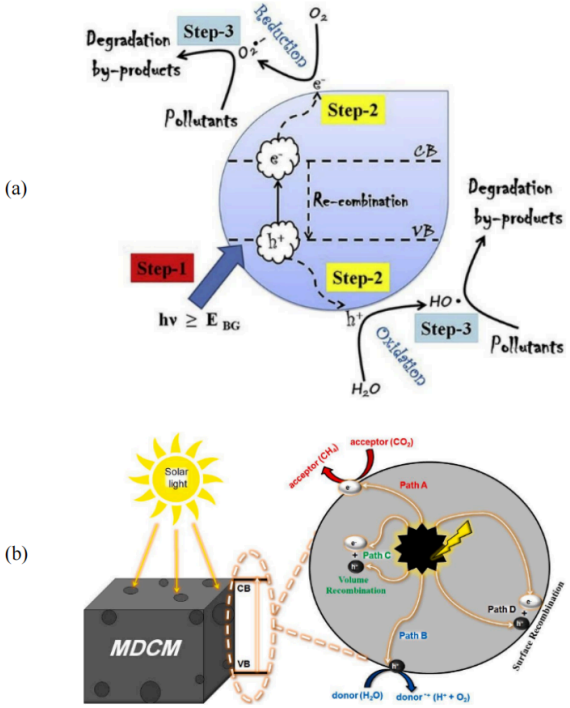


Figure 1. (a) Schematic diagram of semiconductor photocatalysis principle. (b) Schematic diagram of the mechanism and pathway of the surface photocatalytic process of MOF-derived carbon materials (MDCMs)

A typical photocatalytic reaction includes the following processes (as shown in Figure 1(a)): (1) excitation and separation of photogenerated carriers; (2) transfer of electrons and holes; and (3) reduction and oxidation reactions of electrons and holes.

$$\text{Photocatalyst} \xrightarrow{h\nu} e^- + h^+ \tag{1}$$

$$e^- + h^+ \rightarrow \text{Heat} \tag{2}$$

$$E_g = E_{CB} - E_{VB} \tag{3}$$

$h\nu$ is the photon energy, h is Planck's constant, which is equal to 6.63×10^{-34}J/s, v is the speed of light (2.99×108 m/s), e^- represents electrons in the conduction band, and h^+ represents holes in the valence band.

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When light with energy greater than the photocatalyst band gap (E_g) Equation (3) strikes the surface of a semiconductor material, electrons (e^-) in the valence band are excited and jump to the conduction band (CB), while holes remain in the valence band (VB), as shown in Equation (1). These two are collectively referred to as photogenerated carriers. They then transfer to the photocatalyst surface, where they oxidize and reduce organic pollutants (Figure 1(b) Path A, B). However, when electrons (e^-) have no acceptors on the photocatalyst surface or when E_g is very narrow, the photogenerated carriers will recombine, releasing heat energy, as shown in Equation (2). These reverse processes are divided into two types: bulk recombination and surface recombination, depending on the location where the photogenerated carrier recombination occurs (Figure 1(b) Path C, D).

In order to improve the effect of photocatalysis, the synergistic effect of combining with other technologies can promote the generation of active free radicals and improve the photocatalytic degradation pathway. For example, Wei et al. [3] used a photocatalytic membrane in a photocatalytic membrane biofilm reactor to first degrade part of toluene into biodegradable intermediates, which were then mineralized by the biofilm. The coupling of photocatalysis and biodegradation calculations improved the toluene removal efficiency. Hu et al. [4] prepared a new catalyst, and the degradation rate of tetracycline (TC) within 5 minutes reached 96.12% under the coupling of photocatalysis and Fenton technology.

2. Bismuth-based photocatalysts

Bismuth-based semiconductors have attracted much attention due to their unique optical properties and Aurivillius structure. Materials such as $BiVO_4$, Bi_2WO_6, $Bi_2O_2CO_3$, Bi_2O_3, BiOX(X = Cl, Br, I) and Bi_2MoO_6 [5,6] have been reported one after another. Compared with other bismuth-based photocatalysts, Bi_2MoO_6 is an orthorhombic perovskite-type composite oxide, which is a composite oxide material with a layered structure. The internal crystal structure is mainly composed of perovskite layers $(MoO_4)^{2+}$ and lamellar $(Bi_2O_2)^{2+}$ layers. According to the different contents of Bi and Mo in the Bi_2MoO_6 component, it can be divided into three crystal phases. Its general chemical formula is $Bi_2O_3 \cdot nMoO_3$. When n = 3, 2, and 1, they are α-$Bi_2Mo_3O_{12}$, β-$Bi_2Mo_2O_9$, and γ-Bi_2MoO_6, respectively [7]. Compared with α-$Bi_2Mo_3O_{12}$ and β-$Bi_2Mo_2O_9$, γ-Bi_2MoO_6 exhibits better photocatalytic activity because γ-Bi_2MoO_6 has more active oxygen, which can provide more active sites for the reaction and promote the progress of the photocatalytic reaction.

The lattice spacing of Bi_2MoO_6 is a=5.618 Å, b=5.626 Å, c=16.625 Å, α=β=γ=90°, and V=525.417 $Å^3$. It is an n-type semiconductor with an adjustable band gap between 2.5 eV and 2.8 eV. According to DFT theoretical calculations, the 2p orbital of O constitutes the valence band of Bi_2MoO_6, and the 6s orbital of Bi and the 3d orbital of Mo together constitute its conduction band, which effectively enhances the visible light capture ability of Bi_2MoO_6 photocatalyst. Due to its outstanding physical and chemical properties, Bi_2MoO_6 has been widely studied in the fields of solar cells, photocatalytic hydrogen production and photocatalytic carbon dioxide reduction [8]. As early as 2005, Yu et al. [9] discovered that Bi_2MoO_6 can photocatalytically decompose water under visible light, thus opening up the research on Bi_2MoO_6 as a photocatalyst. It is a very important photocatalytic material.

BiOCl crystals, a Silleín family ternary compound semiconductor composed of elements from main groups V-VI-VII, have crystal structure parameters of a=b=3.890 Å, c=7.370 Å, α=β=γ=90°, c/a=1.895, V_0=111.52 $Å^3$, and Z=2. BiOCl crystals exhibit a typical zinc-blende (PbFCl-type) tetragonal structure with D4h symmetry and space group P4/nmm. In its crystal structure, [Cl-Bi-O-Bi-Cl] repeating units alternate along the c-axis through weak van der Waals interactions between Cl

DOI: 10.54254/2755-2721/2026.KA27955

atoms. Density functional theory (DFT) calculations indicate that BiOCl is a UV-excitable, indirect bandgap p-type semiconductor with a band gap of approximately 3.37 eV. Its valence band is primarily formed by the hybridization of Cl 3p orbitals and O 2p orbitals, while the conduction band is formed by Bi 6p orbitals, effectively promoting photocatalytic reactions. BiOCl has been widely used in photocatalytic technology. Wu et al. [10] used a solvothermal method to combine BiOCl and $CuBi_2O_4$ to construct a novel S-type heterojunction photocatalyst. Under visible light irradiation, the catalyst exhibited excellent photocatalytic performance in removing diclofenac aqueous solution (DCF) and degrading gaseous nitric oxide (NO). Yang et al. [11] combined ultraviolet-driven BiOCl and visible-light-driven Bi_2WO_6 to construct a Z-type heterojunction photocatalyst $BiOCl/Bi_2WO_6$. Under visible light irradiation, the heterojunction was able to generate a large amount of H^+, O^{2-}, and OH active radicals to catalyze the degradation of gaseous toluene, with a removal rate of 99.73% within 180 minutes.

3. Photocatalyst modification methods

3.1. Morphology control

The crystal size and micromorphology of a material are key factors affecting its photocatalytic performance. Constructing catalysts with high specific surface area and unique morphology is an effective strategy for regulating the light absorption range and photocatalytic efficiency. This enhancement effect is mainly attributed to two factors: the expanded specific surface area creates a rich network of active sites for surface catalytic reactions; secondly, according to the carrier diffusion kinetics formula (4), the reduction in particle size can effectively shorten the diffusion path of photogenerated electron-hole pairs, thereby significantly improving the charge separation efficiency.

$$\pi = r^2/(\pi^2 D) \tag{4}$$

where τ represents the average time for charge carriers to migrate from the bulk to the surface, D is the diffusion coefficient, and r represents the particle radius.

The synergistic mechanism of these two factors jointly promotes the improvement of photocatalytic activity. At present, the morphologies of Bi_2MoO_6 semiconductor materials that have been developed include nanosheets, rods, flower-shaped hollow spheres, etc.

3.2. Crystal surface engineering

As an important way to improve the performance of semiconductor photocatalysts, the crystal plane regulation strategy is based on the precise design of the synthesis process to achieve directional exposure of the crystal plane. By introducing structure-directing agents (such as surfactants), adjusting reaction conditions, and performing selective etching and other growth control techniques, the crystal planes with specific surface structures are promoted to achieve preferential growth. When the electron-hole pairs generated by photoexcitation migrate to the surface during the reaction, due to the difference in surface potential between different crystal planes, a crystal plane heterojunction with a band structure gradient is spontaneously formed. This charge spatial separation effect based on crystal plane energy band matching significantly reduces the recombination probability of carriers. By constructing such a self-driven charge transfer channel between crystal planes, the

DOI: 10.54254/2755-2721/2026.KA27955

directional migration and efficient separation of photogenerated carriers can be achieved, thereby greatly improving the photocatalytic performance.

3.3. Element doping

Element doping is an effective means to improve the catalytic performance of semiconductor photocatalysts. By doping specific elements into photocatalytic materials, their photoelectric properties can be adjusted. These doping elements change the electronic structure and optical properties of the material by introducing doping energy levels or generating defect vacancies. When the atoms of the introduced elements replace the sites of the main component atoms in the original catalyst, new intermediate energy levels are usually generated in the band gap of the semiconductor, which reduces the energy required for photogenerated carrier excitation and reduces the probability of carrier recombination. Therefore, element doping can cause the catalyst to undergo the following changes: (1) the light absorption range is extended to longer wavelengths; (2) the separation efficiency of electron-hole pairs is improved; (3) the conductivity is enhanced; and (4) the affinity for surface chemicals is improved. In addition, doping may also affect the lattice structure of the catalyst and thus change its morphology and specific surface area.

3.4. Heterogeneous structure construction

In recent years, constructing heterostructures composed of different types of semiconductor materials has become a research hotspot in the field of photocatalysis. One of the key factors that significantly enhances the photocatalytic activity of heterostructures is that the mutual contact of different semiconductor materials leads to the formation of a built-in electric field (IEF). After the photogenerated carriers are excited under external light, the built-in electric field can promote the separation of photogenerated electrons and holes and accelerate the migration of photogenerated electrons to the catalyst surface. In this way, the recombination of electrons and holes is effectively suppressed, significantly improving the photocatalytic efficiency. At the same time, this structural design also broadens the light absorption range of the catalyst, allowing the catalytic reaction to proceed over a wider spectral range. In summary, the design of the heterostructure not only optimizes the electronic properties of the photocatalyst, but also provides more ideal conditions for achieving efficient photocatalytic reactions.

3.5. Element ratio adjustment

To address the shortcomings of bismuth-based semiconductors and their lack of visible light absorption, the strategy of constructing novel bismuth-rich catalysts by adjusting the bismuth content has attracted research interest from researchers both domestically and internationally. This modification method can introduce oxygen vacancies into the catalyst while simultaneously altering the number and orientation of bonds within the crystal. For example, DFT calculations of the crystal face composition of layered $Bi_{12}O_{17}Cl_2$ revealed that the presence of a lone pair of electrons in Bi^{3+} leads to an asymmetric crystal structure, with one additional $[BiO_{2.25}]$ compared to the face structure of BiOCl. This significantly alters the bonding pattern between Bi^{3+} and O^{2-}, with the covalent bond between Bi^{3+} and O^{2-} exhibiting significant anisotropy. The introduction of $[Bi_3O_{4.25}]$ imparts greater asymmetry to the center of the $Bi_{12}O_{17}Cl_2$ crystal structure. The uneven charge distribution between the layers promotes atomic and orbital polarization, which in turn generates an internal electric field

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(IEF) perpendicular to the [$Bi_3O_{4.25}$] and [Cl] layers. The following formula shows that the intensity of IEF depends on the exposure ratio of the (001) direction crystal plane:

$$F_\varepsilon := \left(-2V\rho/\varepsilon\epsilon_0\right)^{1/2}. \tag{5}$$

Fs is the built-in electric field strength; Vs is the surface voltage; and ρ is the charge density. Vs and ρ are proportional to the (001) plane exposure rate.

We have compiled application examples of various modification methods in recent years to improve the photocatalytic degradation effect. For detailed information, please refer to Table 1.

Table 1. Different modification methods improve the degradation effect of catalysts

Method	Photocatalytic materials	Remark	Ref.
Morphology control	Flower-like microspheres Bi_2MoO_6	500W xenon lamp, the degradation efficiency of 5 mg/L RhB solution is 98.4%	[12]
	Hollow Bi_2MoO_6nanorods	Complete degradation of RhB dye within 60 min.	[13]
	(1D)α-Fe_2O_3/Bi_2MoO_6	The degradation rate of MB within 4 h was approximately 65.6%.	[14]
Crystal surface engineering	Bi_2MoO_6 (010)	Fine-tuning the band gap of Bi_2MoO_6 from 2.30 eV to 2.57 eV.	[15]
	Bi_2MoO_6 oxygen vacancies	The removal rate of NO under visible light can reach 43.5%.	[16]
Element doping	BiREMoO$_6$(RE=Pr, Nd, Sm, Tb, Yb)	The band gap was adjusted from 2.99 eV to 2.19 eV.	[17]
	Pt/Bi_2MoO_6	Higher degradation efficiency for 2,4-dibromophenol (DBP).	[18]
Heterogeneous structure construction	$Bi_{12}GeO_{20}$/γ-Bi_2MoO_6 Z-type heterojunction	Good degradation effect on both MBT and TC.	[19]
	Bi_2MoO_6/Bi_5O_7I Z-type heterojunction	Complete inactivation of E. coli (108 CFU/mL) after 90 min.	[20]
	$CuBi_2O_4$/$CdMoO_4$ Z-type heterojunction	The degradation rate of dye MB is as high as 95.36%.	[21]

4. Conclusion

This article takes Bi_2MoO_6 and BiOCl, two bismuth-based photocatalysts, as examples to explore in detail the relationship between their molecular structure, energy band composition and photocatalytic performance. Various modification methods are discussed in detail to improve their photocatalytic performance, and in-depth research and mechanism analysis are conducted on different modification methods. I personally believe that modifying photocatalysis by constructing heterojunctions has broader research value and application prospects. By combining photocatalytic materials with different energy band structures to form different types of heterojunctions, some limitations of the original materials in photocatalysis can be improved, such as increasing the utilization rate of visible light by expanding the light absorption range of the catalyst, and reducing the recombination rate of photogenerated carriers to improve photocatalytic efficiency. In addition, the construction of heterojunctions can also be combined with other modification methods to improve photocatalytic performance through a variety of modification methods.

DOI: 10.54254/2755-2721/2026.KA27955

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