Research progress of MOF/Bismuth-based semiconductor composites in photocatalytic technology

Zhehua Du

Wuhan Second Ship Design and Research Institute, Wuhan, Hubei, 430205, China

Abstract. Photocatalysis has significant potential for environmental remediation and energy conversion, with a focus on designing and developing highly efficient photocatalysts. Composite materials consisting of bismuth-based semiconductors and metal-organic frameworks (MOFs) exhibit outstanding photocatalytic activity, and have garnered significant attention from researchers as a highly sought-after material. A review is conducted on recent advances in MOF/bismuth-based semiconductor composites. On this basis, the synthesis methods of MBCs are described in detail, and then the applications of MBCs in organic pollutant degradation, Cr (VI) reduction, water (H2O) splitting, nitrogen (N2) fixation discussed. Finally, this paper highlights the current challenges in photocatalysis using MBCs and provides insights into the future development direction for MBCs photocatalysis technology. The preparation and modification methods of MBCs, the improvement of photocatalytic efficiency, the mechanism of oxidative degradation of organic matter and the mechanism of photocatalytic complete hydrolysis of water need further study.

1. Introduction

Since the photocatalytic process uses abundant and sustainable solar energy or light energy to catalyze the reaction, photocatalytic technology has developed rapidly in recent years and is widely used in environmental remediation and energy conversion. However, many photocatalytic materials face challenges such as wide band gap, rapid recombination of electron-hole pairs and low utilization of visible light. As a consequence, they exhibit low photocatalytic efficiency and hinder the practical application of photocatalytic technology in engineering.

Due to MOFs unique properties such as ultra-high specific surface area, stable porous structure, and changeable functionality, it has been widely used in the fields of gas adsorption and separation, sensing, biomedicine, proton conduction and catalysis. As a new visible light responsive photocatalyst, bismuth-based semiconductor has a band gap between 2.0eV and 3.0eV, which is considered to be suitable for removing pollutants from environmental media and catalyzing the synthesis of new energy source [1].

This paper reviews the various preparation methods of MBCs at home and abroad in recent years and the application progress in environmental remediation and energy conversion, in order to provide new ideas for the large-scale promotion and application of photocatalytic technology.

Corresponding author's e-mail: shunli878@163.com

2. Preparation of MBCs

According to the preparation process of various MBCs photocatalysts reported in the current literature, the preparation methods can be mainly summarized into two categories. One method is to prepare MOFs materials by hydrothermal/solvothermal, electrochemical, ultrasonic, microwave and other pretreatment methods, and then to prepare MBCs by combining MOFs with bismuth-based semiconductors through hydrothermal/solvothermal processes. Another method is to make MOFs and bismuth-based semiconductor materials react at low temperature based on high-energy ball milling, and then form MBCs composites [2]. Figure 1 is a scanning electron microscope image of BiOBr/NH2-UiO-66 (BUN) hybrid composite prepared by hydrothermal method [3].

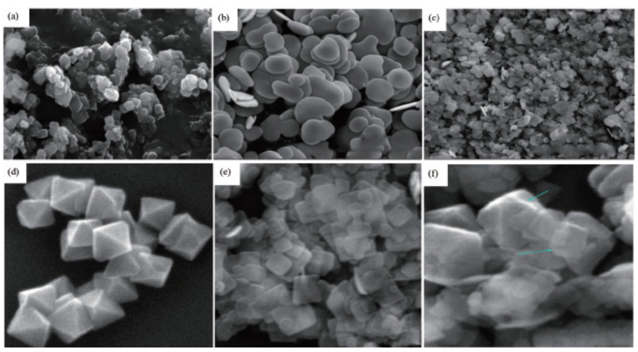

Figure 1. SEM images of BiOBr/NH2-UiO-66

3. Application of MBCs photocatalysis

Metal-organic frameworks (MOFs) are a new type of crystalline porous materials formed by self-assembly of metal ions or clusters as nodes and organic ligands as linkers through the coordination of the two. It is one of the research hotspots in recent years. At present, in order to solve the shortage of fast recombination of photogenerated hole-electron pairs in intrinsic bismuth-based semiconductors, modification is usually carried out through strategies such as component adjustment, morphology control and construction of heterojunction structures. Based on the microstructure and optical properties of bismuth-based semiconductors and MOFs, MOFs/bismuth-based semiconductor composites (MBCs) can be designed to combine the advantages of the above two materials. In recent years, the photocatalysis application reports of MBCs have increased year by year, mainly for environmental restoration and energy conversion. The specific applications are shown in Table 1.

Table 1. Application of MBCs in photocatalysis

Application	Catalyst	References
RhB degradation	$BiOBr/UiO\text{-}66\text{-}NH_2$	[4]
RhB degradation	$MIL\text{-}125/BiVO_4$	[4]
RhB degradation	$Bi_2WO_6/UiO\text{-}66$	[4]
CV degradation	$BiVO_4$/MIL-100(Fe)	[5]
AB92 degradation	MIL-88A(Fe)/BiOI	[5]
MTZ/CFX degradation	$CuWO_4/Bi_2S_3/ZIF\text{-}67$	[5]
CBZ/TC degradation	MIL-53(Fe)/BiOBr	[5]
BPA/TC degradation	NH_2-MIL-125/BiOCl	[5]
TC degradation	$BiOI/NH_2\text{-}UiO\text{-}66/g\text{-}C_3N_4$	[6]
TC degradation	$UiO\text{-}66/BiVO_4$	[6]
TC degradation and Cr (VI) reduction	NH_2-UiO-66/BiOBr	[5]
Cr (VI) reduction	$BUC\text{-}21/Bi_{24}O_{31}Br_{10}$	[5]
Cr (VI) reduction	MIL-53(Fe)/$Bi_{12}O_{17}C_{l2}$	[5]
Cr (VI) reduction	$Bi1_2O_{17}C_{l2}$/MIL-100(Fe)	[6]
Photolysis water	NH_2-MIL-125(Ti)@Bi_2MoO_6	[6]
Photolysis water	MIL-100(Fe)/$BiVO_4$	[5]
Nitrogen fixation	$ZIF\text{-}8/Bi_4O_5Br_2$	[6]
Nitrogen fixation	$MIL\text{-}100/Bi_4O_5Br_2$	[7]
CV degradation	UiO-66/MIL-100(Fe)	[7]

3.1 Environmental remediation application

3.1.1 Dye degradation. With the development of industry, nearly 800,000 tons of dye wastewater lacking pretreatment are discharged directly into the water body every year. The dyes in the water body will not only cause toxic effects such as allergy, dermatitis, nausea, etc., but also have genotoxic and teratogenic, carcinogenic, mutagenic effects. MBCs composites have excellent photocarrier separation and migration efficiency and broad-spectrum light absorption ability. Bibi [7] deposited BiOBr on the surface of $UiO\text{-}66\text{-}NH_2$ by hydrothermal treatment to form a more compact $BiOBr/UiO\text{-}66\text{-}NH_2$ composite heterojunction structure. After being exposed to visible light for 2 hours, the degradation efficiency of rhodamine B was 83%. Yang [8] The MOF-5 / BiOBr composite material was prepared by ultrasonic method. The photocatalytic degradation of methyl orange showed that the introduction of MOFs components can effectively improve the photocatalytic performance of intrinsic bismuth halide oxide.

3.1.2 Degradation of pharmaceutical and personal care products (PPCPs). PPCPs is one of the emerging environmental pollutants. With the growth and wide application of PPCPs, a variety of persistent organic pollutants such as antibiotics and endocrine disruptors have been commonly detected in various water environments and soil sediment. Hu [8] prepared NH_2-MIL-125(Ti)/BiOCl composite (NM/BOC) by one-step hydrothermal method. The photocatalytic degradation experiment of tetracycline (TC) shows that the catalytic effect of NM/BOC-10 is the best, which is 3.5 times and 35 times the activity of pure BiOCl and pure NH_2-MIL-125 (Ti), respectively. As shown in Figure 2, Tang et al. [9] prepared BiOBr/MIL-53 (Fe) composite material (BM) by solvothermal method. BM-20 can degrade 85% carbamazepine under visible light irradiation for 100 min. Its degradation kinetic constant is 15 times that of pure BiOBr and pure MIL-53(Fe). Liang [9] prepared a ternary heterojunction BiOI@UIO-66 (NH2) @ g-C3N4 (BiOI@UNCN) by solvothermal-hydrothermal method. Among them, BiOI@UNCN-40 (the mass fraction of BiOI is 10%) has the best photocatalytic effect on TC, and can degrade 80% TC within 180 minutes. The degradation dynamics constants are 18.42, 4.41, 3.06 and 2.59 times of UIO-66 (NH_2), UNCN, BiOI and BiOI@UNCN-20, respectively.

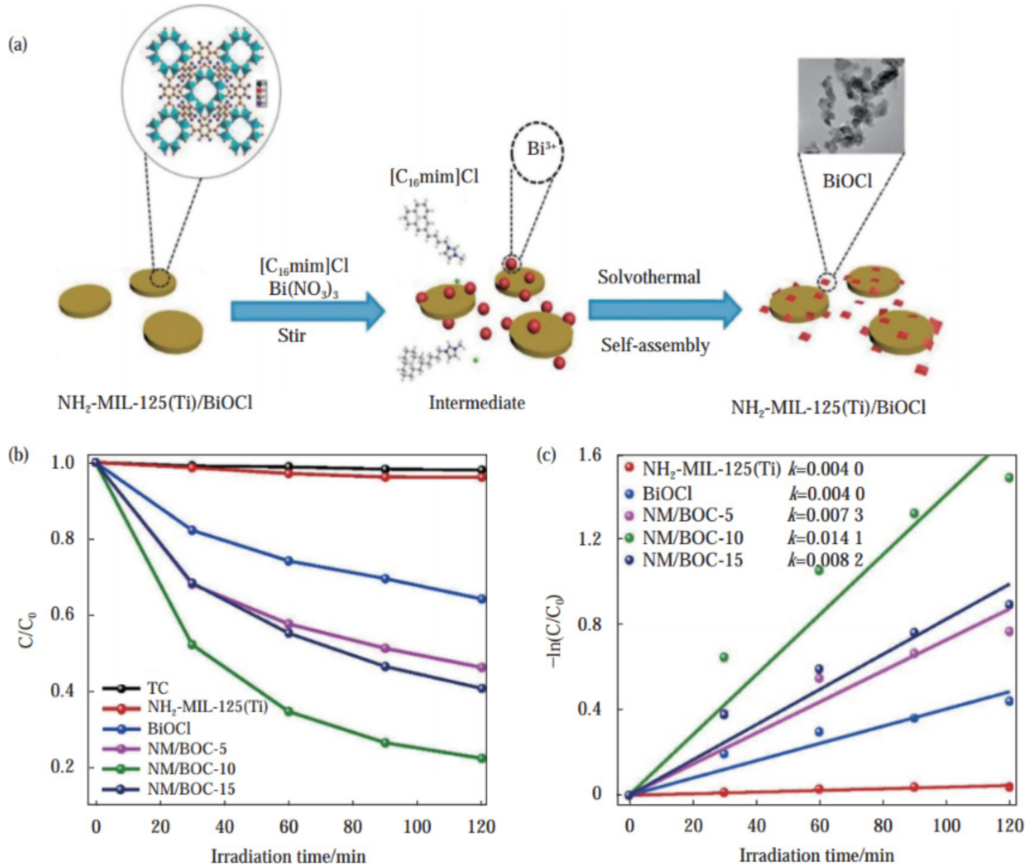

Figure 2. NH_2-MIL-125(Ti)/BiOCl composites

3.1.3 Photocatalytic reduction of Cr (VI). Hexavalent chromium (Cr (VI)) comes from industrial wastewater of tannery, electroplating, printing, pigment and other manufacturing industries. It has the characteristics of ultra-high toxicity, carcinogenicity and high solubility. Zhao [10] synthesized $Bi_{24}O_{31}Br_{10}$ by hydrothermal method for the first time. The experiment of reducing Cr (VI) in FIG. 3 shows that when the mass ratio of $Bi_{24}O_{31}Br_{10}$ to BUC-21 is 1: 1 (BB-100), the catalytic effect is the best.

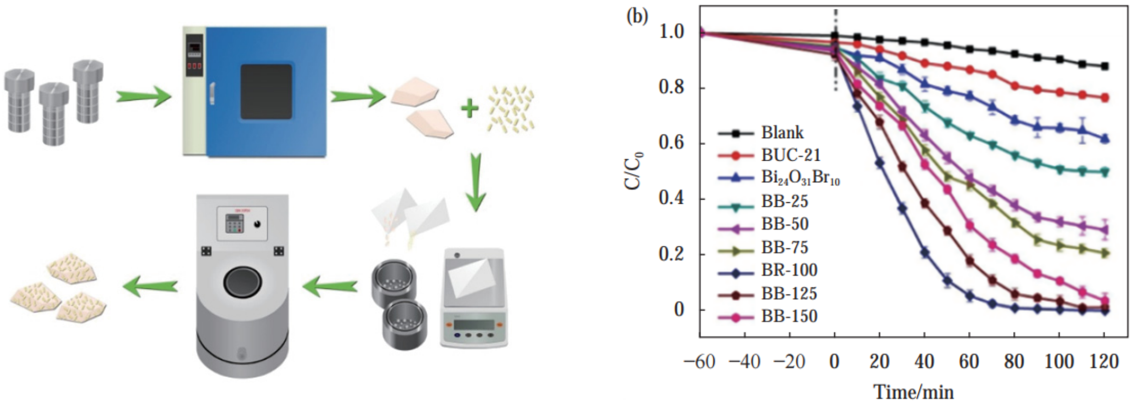

Figure 3. BUC-21/$Bi_{24}O_{31}Br_{10}$ composites

3.2 Energy conversion application

3.2.1 Photocatalytic decomposition of water. Photocatalytic decomposition of water technology for hydrogen production can transform solar energy into renewable and clean energy, thus effectively breaking the bottleneck of energy shortage [9]. The efficiency of photolysis water is mainly limited by the slow oxygen evolution kinetics. Han prepared a new composite material MIL-100(Fe) @ $BiVO_4$ by hydrothermal in situ growth of MIL-100 (Fe) nanoparticles on the surface of decahedral $BiVO_4$. The experiment of photocatalytic decomposition of water shows that when the load of MIL-100(Fe) is 8%, MIL-100(Fe)@$BiVO_4$ composite exhibits the best photocatalytic oxygen evolution performance, which is 4.3 times the catalytic activity of pure $BiVO_4$. The improvement of the photocatalytic performance is mainly due to the formation of a tight heterojunction

https://doi.org/10.1051/e3sconf/202338504034

interface between MIL-100(Fe) and $BiVO_4$, which promotes the effective transfer and conduction of carriers between the bifunctional components.

3.2.2 Photocatalytic ammonia synthesis. In order to solve global energy and environmental problems, an artificial photosynthesis system that can use solar energy is essential. Ammonia, as a raw material of chemical fertilizer and a potential hydrogen carrier and fuel, is an indispensable energy substance in modern industrial agriculture [10]. Traditional synthetic ammonia uses Haber - Bosch process. It not only requires a high temperature of 400°C - 600°C and a high pressure environment of 20 MPa -40MPa, but also produces a large amount of carbon dioxide emissions in the process of ammonia synthesis [8].

It is a green and sustainable method to synthesize NH_3 by using N_2 and H_2O at normal temperature and pressure based on photocatalytic technology. Liu [**9**] The hydrophilic $Bi_4O_5Br_2$ deposited on a hydrophobic surface of ZIF-8, $Bi_4O_5Br_2$ / ZIF-8 composite photocatalyst having a gas-liquid-solid three-phase reaction interface. The photocatalytic synthesis rate of NH_3 is 327.338 μ mol • L^{-1} • h^{-1} • g^{-1}, which is 3.6 times the synthesis efficiency of $Bi_4O_5Br_2$. The source of this excellent activity is that the unique three-phase interface structure enables N_2 to be transported directly from the gas phase to the photocatalytic reaction interface, replacing the process of N_2 diffusion through the liquid phase. This rapid supply of N_2 can effectively capture photogenerated electrons, thereby improving the utilization efficiency of photogenerated electrons and nitrogen fixation activity. The mechanism diagram is shown in Figure. 4.

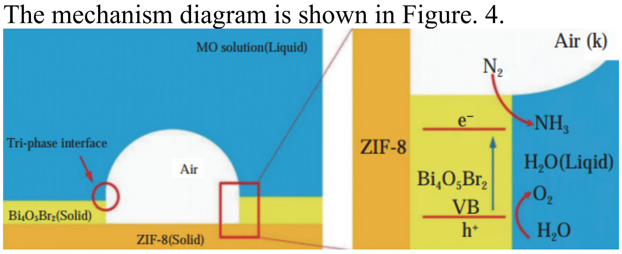

Figure 4. Nitrogen fixation mechanism

4. Conclusion

This paper reviews the two main preparation methods of MBCs and their applications in the fields of photocatalytic environmental remediation and energy conversion, mainly including the degradation of organic dyes, the degradation of PPCPs and Cr (VI) reduction, photodecomposition of water to produce hydrogen and synthesis of ammonia. In general, the construction of MBCs composite structure increases the activity check point of catalytic reaction, expands the spectral range and inhibits photogenerated carrier recombination, thereby improving the photocatalytic performance. However, further research on MOFs/ bismuth based composites is still needed. In particular, the preparation and modification methods of MBCs, the improvement of photocatalytic efficiency, the mechanism of oxidative degradation of organic matter and the mechanism of photocatalytic complete hydrolysis of water need further study.

- In the field of photocatalytic environment remediation and energy conversion, the research on the efficiency of photocatalysis, the efficiency of oxidative degradation of organic matter, and the speed of photocatalytic total hydrolysis all rely on the improvement of the photocatalytic performance of MBCs.
- So far, the preparation methods of MBCs are still not perfect. Neither hydrothermal / solvothermal method nor ball milling method has its shortcomings. Hence, it is imperative to investigate novel approaches to enhance the manufacturing process of MBCs. Scholars should open up ideas, not rigidly adhere to the existing preparation methods, and boldly develop innovative preparation technologies.
- Currently, MBCs are usually prepared with organic solvents and treated at high temperatures. Hence, it is imperative to assess the environmental ramifications of different preparation techniques for MBCs. If the organic solvent and high temperature are not treated well, it will have a negative impact on the environment.

References

1. Liang Q. (2019) Surfactant - assisted synthesis of photocatalysts: mechanism, synthesis, recent advances and environmental application. Chemical Engineering Journal, 372:429-451.
2. Zhu J. (2019) A turn-on MOF-based luminescent sensor for highly selective detection of glutathione. Journal of Solid State Chemistry, 270:317-323.
3. Zhao C. (2021) 1+1>2: a critical review of MOF/bismuth-based semiconductor composites for boosted photocatalysis. Chemical Engineering Journal, 417:128022.
4. Bibi R. (2018) Hybrid BiOBr/ IOI-66-NH2 composite with enhanced visible-light driven photocatalytic activity toward RhB dye degradation. RSC Advances, 8(4): 2048-2058.
5. He Y.P. (2019) Short and photocatalytic properties of Bi_2WO_6/UiO-66 composite. Chinese Journal of Inorganic Chemistry, 35(6): 996-1004.
6. Li J.M. (2020) Photocatalytic degradation of crystal violet using BiVO4/MIL-100(Fe) composites. Fine Chemicals, 37(1): 33-38.
7. Liang Q. (2018) Fabrication of BiOI@UIO-66(NH_2)@g-C_3N_4 ternary Z-scheme heterojunction with enhanced visible-light photocatalytic activity. Applied Surface Science, 456:899-907.
8. Qi Y.W. (2021) Preparation of UiO-66/$BiVO_4$ composite photocatalyst and its photodegradation of tetracycline. China Environmental Science, 41(3): 1162-1171.
9. Blakemore J.D. (2015) Molecular catalysts for water oxidation. Chemical Reviews, 115 (23): 12974-3005.

10. Wang L. (2018) The Greening ammonia toward the solar ammonia refinery. Journal of Joule, 2(6) :1055-1074.