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Research Progress on Modification Strategies of MIL-101(Fe) -based Photocatalysts

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Abstract: Emerging pollutants, due to their toxicity, persistence, and bioaccumulation, pose a serious threat to ecosystems and human health. Tetracycline hydrochloride (TCH) is a widely used antibiotic that is frequently detected in water bodies and wastewater, necessitating efficient degradation technologies. Photocatalytic technology can achieve deep mineralization of organic pollutants, representing a green and sustainable treatment approach. Among various photocatalysts, the iron-based metal-organic framework MIL-101(Fe) has attracted attention due to its visible light response, high specific surface area, and good water stability. However, pure-phase MIL-101(Fe) faces issues such as a narrow visible light absorption range, rapid recombination of photogenerated charge carriers, and insufficient active sites. This paper systematically reviews modification strategies to enhance the photocatalytic performance of MIL-101(Fe), including the construction of bimetallic MOFs, heterostructures, ion doping, and defect engineering. These strategies can broaden the light absorption range, promote charge separation, and increase active centers. Finally, future research directions are discussed, such as green synthesis, long-term stability evaluation, mechanism studies, and the extension of photocatalytic removal to other emerging pollutants.

Keywords: MIL-101(Fe); Photocatalysis; Modification Strategies; Emerging Pollutants

1. Introduction

1.1 Overview of Emerging Pollutants

With the rapid development of modern chemical industry, the types and production of synthetic chemicals are increasing day by day, which has also led to new environmental problems. Emerging pollutants (EPs) refer to toxic and harmful chemicals that possess characteristics such as biological toxicity, environmental persistence, and bioaccumulation, and pose significant risks to ecosystems or human health after entering the environment, but have not yet been included in environmental management or are inadequately addressed by existing management measures [1]. Emerging pollutants have three important characteristics: high biological toxicity, environmental persistence, and bioaccumulation [1]. Among the 219 million chemical substances registered worldwide, less than 1% are under environmental regulation. Their main sources include industrial production, daily life, and agricultural activities, covering four major categories: persistent organic pollutants, endocrine disruptors, antibiotics, and microplastics.

1.2 Tetracycline Hydrochloride

Tetracycline hydrochloride is a broad-spectrum antibiotic with the chemical formula $C_{22}H_{25}ClN_2O_8$, consisting of a core structure of four fused benzene rings. Its aqueous solution stability is affected by pH, light, and temperature. TCH is widely used in human medicine, animal husbandry, and aquaculture, and is the second most used class of antibiotics globally. The detection rates of antibiotics in Chinese soil, surface water, and coastal waters reach 100%, 98.0%, and 96.4%, respectively [2]. The concentration of TCH in pharmaceutical wastewater can reach 32.0 mg/L, and in livestock and poultry wastewater about 31.05 μg/L [3,4]. Once TCH enters the environment, it can induce bacteria to produce resistance genes (tet genes) and spread through horizontal gene transfer, posing a serious threat to public health.

1.3 Traditional Governance Techniques

Traditional TCH wastewater treatment

technologies include physical adsorption, biological methods, and advanced chemical oxidation. Adsorption only achieves phase transfer of pollutants, biological methods are easily inhibited by the toxicity of antibiotics and may induce the spread of resistance genes, and conventional chemical methods may generate more toxic disinfection by-products [5,6]. Therefore, there is an urgent need to develop efficient, green, and sustainable advanced treatment technologies.

2. Photocatalytic Technology

2.1 Introduction to Photocatalysis Technology

Photocatalytic technology, with semiconductor materials at its core, generates highly oxidative and reductive active species through light excitation to achieve deep mineralization of organic pollutants. Its advantages include mild reaction conditions, thorough mineralization, the ability to utilize sunlight, and environmental friendliness. Since Fujishima and Honda discovered the decomposition of water by TiO_2 photoelectrodes in 1972, photocatalytic technology has developed rapidly [7].

2.2 Basic Mechanism of Photocatalytic Degradation

Photocatalytic degradation includes three processes: (1) Excitation of photogenerated charge carriers: when the photon energy is greater than or equal to the band gap, electrons jump from the valence band to the conduction band, generating electron-hole pairs; (2) Separation and migration of charge carriers: electrons and holes migrate to the surface, with some recombining; (3) Surface redox reactions: electrons reduce O_2 to form $\cdot O_2^-$, and holes oxidize H_2O or OH^- to form $\cdot OH$. These reactive oxygen species gradually mineralize pollutants into CO_2 and H_2O.

2.3 Overview of Traditional Photocatalysts

Traditional photocatalysts are mostly based on semiconductor materials, including TiO_2, ZnO, $g\text{-}C_3N_4$, bismuth compounds, silver salts, and metal sulfides. Each material has its own advantages and disadvantages.

(1) TiO_2: Due to its high activity under ultraviolet light, chemical stability, abundant reserves, low cost, and non-toxicity, it has become the most extensively studied photocatalyst. However, its wide band gap (anatase ~3.2 eV, rutile ~3.0 eV) limits it to only responding to ultraviolet light (which accounts for less than 5% of the solar spectrum), and the photogenerated charge carriers are prone to recombination [8].

(2) ZnO: ZnO is an n-type semiconductor with a wide band gap (3.37 eV) and high exciton binding energy (60 meV), and it is low-cost and environmentally friendly. However, ZnO suffers from serious photochemical corrosion under light, resulting in poor stability [8].

(3) $g\text{-}C_3N_4$: As a non-metal polymer semiconductor, $g\text{-}C_3N_4$ has advantages such as visible light response (band gap about 2.7 eV), good thermal stability, and simple preparation. However, its intrinsic defects include high carrier recombination rates and slow exciton dynamics, leading to relatively low photocatalytic activity [9].

(4) Bismuth-based photocatalysts: Materials such as $BiVO_4$ (band gap about 2.4 eV) and Bi_2WO_6 have good visible light responses. However, pure bismuth-based catalysts generally have high electron-hole recombination rates, low quantum yields, and limited light absorption capabilities.

(5) Silver-based photocatalysts: Ag_3PO_4 has extremely high quantum efficiency under visible light. But its severe photochemical corrosion (reduction to metallic Ag), high silver cost, and potential leaching that may cause secondary pollution limit its practical applications [10].

(6) Metal sulfides: CdS has a narrow band gap (~2.4 eV) and a relatively negative conduction band position, making it suitable for visible light photocatalysis. However, metal sulfides are prone to photochemical corrosion ($S^{2-} \rightarrow S^0$), and the toxicity of heavy metals like cadmium poses environmental risks [11].

In summary, traditional photocatalysts face common problems: low solar energy utilization, rapid carrier recombination, and insufficient stability. Therefore, there is an urgent need to develop new photocatalytic materials with novel structures and excellent performance. In this context, metal-organic frameworks (MOFs) have become a promising platform due to their high specific surface area, tunable structure, and diverse functionalities.

3. Introduction to MIL-101(Fe)

MIL-101(Fe) belongs to the MIL series of iron-based MOFs and was first developed by the team at the Lavoisier Institute in France. It uses trivalent iron ions (Fe^{3+}) as metal nodes and terephthalic acid (H_2BDC) as the organic ligand, forming a three-dimensional porous structure with MTN topology. Its structure contains two types of mesoporous cages (pore sizes approximately 2.9 nm and 3.4 nm), which are connected by microporous windows (about 1.2–1.6 nm) to form a three-dimensional pore network. This unique pore structure gives it a large specific surface area (typically 400–600 m^2/g) and pore volume, facilitating the diffusion and enrichment of reactant molecules. The material has high thermal stability (decomposition temperature >300°C) and excellent hydrothermal stability, maintaining the framework integrity over a wide pH range.

In photocatalytic research, MIL-101(Fe) has attracted much attention compared to MOFs containing expensive or toxic metals such as chromium, due to its low cost, abundant availability, visible light response, environmental friendliness, and good hydrothermal stability [12]. Many studies have reported its application in the degradation of organic pollutants under visible light.

The photocatalytic potential of MIL-101(Fe) depends on the organic ligands and iron centers that absorb visible light. LMCT is the most common charge transfer mode in MOFs and an effective mechanism to prevent electron-hole recombination [13]. Under light irradiation, the Fe-O clusters can be directly photoexcited to generate electron-hole pairs. At the same time, due to the LMCT mechanism, the organic ligands in Fe-MOFs can also be excited as light-harvesting antennas to generate electrons. The photogenerated electrons then transfer from the LUMO of the ligands to the LUMO of the Fe-O clusters, and subsequently to the material surface to participate in reactions [14]. LMCT achieves better electron-hole separation through spatial separation from the ligand to the metal [13]. Compared with wide-bandgap semiconductors, this LMCT mechanism enables MIL-101(Fe) to respond to visible light, expanding the utilization range of solar energy.

4. Photocatalytic Modification Strategies Based on MIL-101(Fe)

4.1 Limitations of MIL-101(Fe)

The monometallic MIL-101(Fe) also faces performance bottlenecks in the photocatalytic degradation of pollutants, mainly due to intrinsic structural limitations at the atomic and molecular scales. The electronic structure of this material is dominated by a single iron metal center, and its relatively fixed coordination environment and energy levels result in a light absorption range mostly confined to the ultraviolet and part of the visible spectrum (band gap approximately 2.5-3.0 eV), leading to low visible light utilization. Moreover, photogenerated electron-hole pairs are prone to recombination due to a weak built-in electric field, resulting in low charge separation efficiency and affecting photocatalytic performance [15]. In addition, the active sites composed of single Fe-O clusters have a relatively uniform local chemical environment, with limited adsorption selectivity and activation capability for pollutants. At the same time, mass transfer within the material's pores may become a limiting factor due to pore blockage, preventing some internal active sites from fully participating in reactions [16]. These factors all restrict the overall catalytic efficiency of the material, necessitating breakthroughs through modification strategies.

4.2 Modification Strategies

(1) Construction of bimetallic metal-organic frameworks

Bimetallic metal-organic framework (MOF) materials have large specific surface areas, synergistic effects of the two metals, and tunable multi-components and morphologies, which are beneficial for increasing porosity, enhancing active sites, and improving electron transfer rates. These advantages make bimetallic MOF materials have potential applications in various fields such as adsorption, sensing, and energy. Meanwhile, in addition to the excellent application performance of bimetallic MOF materials themselves, they can also be used as precursors for further modification, and their derivatives can maintain the morphology before and after modification. Metal-organic framework materials, through precise control of the ratio and spatial configuration of two metal ions [17], achieve a significant enhancement of MOF performance and demonstrate great potential in the field of photocatalysis.

(2) Heterostructure construction

For an ideal semiconductor photocatalyst, it is necessary to have suitable band edge positions to ensure appropriate redox potentials while also having a narrow bandgap to guarantee more visible light absorption. However, these two requirements are contradictory and difficult to achieve in a single semiconductor photocatalyst. Therefore, constructing composite semiconductor photocatalysts through surface and interface regulation, adjusting the electronic structure, broadening the light absorption range, and ensuring the material's redox capability is the most commonly used strategy. By combining two or more semiconductor materials through various synthesis methods, the resulting composite materials can expand the light absorption range and improve photocatalytic degradation performance. Generally, semiconductor materials with matched energy levels are selected so that electrons can transfer from the conduction band of one material to the conduction band of another within the light absorption range, while holes in the valence band can also transfer according to differences in energy levels, improving the separation efficiency of electron-hole pairs. For MOF-based semiconductor composites, researchers often load metal oxides with good conductivity and light absorption properties, as well as quantum dots, onto the metal framework surface. For example, MOF materials, due to their poor conductivity, are often combined with carbon materials such as graphene and g-C_3N_4, as well as semiconductor materials with good photocatalytic potential such as sulfide- and bismuth-based compounds [18]. This strategy fundamentally addresses the intrinsic defects of difficult photogenerated charge carrier separation through interface engineering with energy band matching.

(3) Ion doping

Doping metal ions into photocatalytic materials can effectively broaden the maximum boundary of light absorption. On one hand, lattice defects caused by ion doping can form trapping centers and inhibit the recombination of electrons and holes; on the other hand, doping creates energy levels, and under lower light intensity, electrons at these doped energy levels can capture more photons, further improving the utilization efficiency of photons. It should be noted that not all metal ions are beneficial for photocatalytic degradation, and dopants should be reasonably selected according to the band structure.

(4) Defect engineering

It is an effective strategy to broaden the light absorption range of photocatalysts, enhance light absorption intensity, and accelerate the separation efficiency of charge carriers. Defects in the MOF lattice can be generated by changing the synthesis parameters of the precursors, synthesis temperature, reaction time, or by adding coordination modulators [19]. Defect structures are usually accompanied by MOF lattice distortion and changes in its related pore structure, also affecting the material's band gap and photocatalytic performance [20]. Arthur's research confirmed the importance of structural defects in enhancing the photocatalytic performance of MOFs; unsaturated sites generated around metal sites provide additional pathways for the migration of photogenerated carriers, promoting their migration and separation, while also enhancing catalytic activity [21].

5. Conclusion and Outlook

In May 2022, China released the "New Pollutant Control Action Plan," marking a new stage in high-standard requirements for new pollutant management. Traditional photocatalytic materials have issues such as low solar energy utilization, rapid charge carrier recombination, and insufficient stability. MIL-101(Fe), with advantages such as structural stability, strong visible light response, and environmental friendliness, is one of the candidate materials for removing new pollutants. Through modification strategies such as constructing bimetallic structures, forming heterostructures, ion doping, and defect engineering, it is possible to effectively broaden the light response range, inhibit charge carrier recombination, and increase active sites, thereby significantly improving photocatalytic performance.

Currently, research is still in the developmental stage. Future focus can be placed on: (1) developing green, cost-effective large-scale synthesis methods; (2) exploring the long-term stability and reusability of modified materials in complex water bodies; (3) combining theoretical calculations with advanced characterization techniques to elucidate the regulatory mechanisms of modification strategies on electronic structure and surface reaction kinetics; (4) expanding the application of MIL-101(Fe)-based materials in the photocatalytic removal of other new pollutants (such as microplastics, endocrine disruptors, etc.). Systematically summarizing the modification strategies of MIL-101(Fe) and their application prospects in photocatalytic removal of new pollutants provides important theoretical guidance and practical value for designing efficient and stable photocatalysts.

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