Preparation of highly efficient photocatalysts based on heterojunction construction of MOFs

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Abstract

Metal-Organic Frameworks (MOFs) are composed of metal ions and organic linkers, and are widely used for catalytic degradation because of their unique physicochemical properties. In recent years, it has become a hot research topic to integrate semiconductor or conductive materials on MOFs to improve the photocatalytic degradation performance of MOFs. This paper introduces the preparation and properties of several common photocatalytic degradation materials of MOFs, and the highly efficient photocatalysts composed of MOFs and semiconductors, and prospects the future development of MOFs derivative materials.

Keywords

MOFs, semiconducto, heterojunction, TiO₂, C₃N₄, ZnO.

1. Introduction

MOFs, with their large spatial and electronic structure diversity in specific surface area due to their tunable porous structure and chemical function, have found important applications in catalysis, storage, separation and drug delivery ^[1]. As a new material with photocatalytic function, MOFs have a wide spectral response range; because they contain different types of sites, such as unsaturated metal ions, substituents on organic ligands, or active species adsorbed in micropores, there is often more than one catalytic synergy ^[2,3]; large specific surface area and high porosity, can provide more active adsorption sites for photocatalytic reaction, and improve the transmission rate of light-generated charge ^[4]. However, its low quantum efficiency and photogenerated carriers are easy to compound, which will affect the photocatalytic efficiency. For this problem, MOFs can be combined with semiconductors to build a heterojunction to improve the efficiency of photocatalyst ^[5]. In this paper, we review the development of MOFs commonly used for photocatalysis, and heterojunction formation constructed by MOFs with TiO₂, C₃N₄, ZnO and other materials, and discuss the future of MOFs derived materials.

Figure 1. Schematic diagram of the metal-organic frame structure

2. Common MOFs of materials

There are many kinds of MOFs materials according to different frames and derivative materials with different preparation methods and raw materials. At present, MIL series, UIO series, PCN series and ZIF series have been prepared successively.

2.1. MIL series

MY ^[6] et al. successfully prepared MIL-88B from dimethylformamide (DMF) and ferric chloride (FeCl₃·6H₂O) and terephthalic acid (H₂BDC) by microwave assisted heating to 150 °C, 10 minutes; scanning electron microscopy (SEM) results showed that the crystals were spindle and dispersed. Then it studied the effects of heating time, heating temperature, and the concentration of MIL-88B-Fe product. With the yield and crystallinity at the heating temperature, the product produced the same MIL-88B crystal phase, but the growth of the crystal surface improved.

MIL-101 (Fe) photocatalyst has the advantages of controlled morphology, simple preparation and large porosity, and has wide application prospects in the fields of visible light degradation of pollutants, photocatalytic reduction of CO_2 and photocatalytic decomposition of water, etc. Wang ^[7] et al. prepared the metal-organic frame material MIL-101 (Fe), adsorbed and removed NO₃-in water, and explored the effects of MIL-101 (Fe) dosage, adsorption time and solution pH value on the adsorption properties of the material.

Wang ^[8] et al. prepared the environmentally friendly MIL-88A (Fe) by using fumarate, ferric chloride, cobalt nitrate hexahydrate and ethanol-water mixture as solvent. The prepared MIL-88A (Fe) has good light-Fenton catalyzed ofloxacin (OFL) degradation. Under visible light irradiation, the OFL degradation efficiency of MIL-88A was 100% at the initial dose of 0.25 g / L and H₂O₂ concentration of 1.0 mL / L in 40 min. Using Na₂EDTA (0.5 mmol/L), IPA (0.5 mmol/L) and 4-benzoquinone (BQ, 0.5 mmol/L), h⁺, ·OH and ·O²⁻ respectively, and obtained that the main active substance produced during light-Fenton oxidation is ·OH radical. Meanwhile, OFL showed that MIL-88A showed good stability and reability under visible light irradiation. The formation mechanism of ·OH radical is defined as equation (1) - (4).

$$MIL-88A + hv \rightarrow h^+ + e^-$$
(1)

$$Fe (III) + H_2O_2 \rightarrow Fe(II) + \cdot HOO + H^+$$
(2)

 $Fe(II) + H_2O_2 \rightarrow Fe(III) + \cdot OH + OH^-$ (3)

$$H_2O_2 + e^- \rightarrow \cdot OH + OH^- \tag{4}$$

2.2. UiO series

UiO-66 is a kind of pick fund organic frame material, because of its octahedral threedimensional crystal structure, so UiO-66 material has excellent stability ^[9]. The high stability, rich pore structure, and flexible and controllable characteristics of UiO-66 make it widely studied in the fields of adsorption and catalysis ^[10]. Wang ^[11] et al. studied the adsorption kinetics of tetraxene at UiO-66-NH₂ by using quasi-first, quasi-secondary and intra-particle diffusion kinetic models to fit the experimental data. The Gibbs free energy, enthalpy and entropy changes of the UiO-66 adsorption process are also calculated. Wang ^[12] et al. doped amino acids into UiO-66 to adsorb anionic dyes. It was found to regulate the crystal form of UiO-66 by amino acids to form a hierarchical structure of micropores and medium pores with high specific surface area. Aminolated UiO-66 also showed more selectivity for anionic dyes, enabling self-adsorption and desorption through pH regulation.

2.3. PCN series

Gold chemistry is not active, corrosion resistance, oxidation resistance, is widely used in jewelry, research laboratories and industrial production. Its presence in water pollution is reported to be caused by industrial wastewater, jewelry making minerals, processing and e-waste ^[13-15]. Nazri ^[16] et al. used SALI method to prepare PCN-222 (PCN-222-MBA) sorbent, so that mesoporous PCN-222 could adsorb gold ions in aqueous medium. The study showed that the maximum adsorption capacity of Au (III) within 1 min can reach 714.3 mg·g⁻¹. In the presence of different metal ions, thiol-functionalized PCN-222 showed significant selectivity for Au (III). And showed stable regeneration in the desorption-adsorption cycle experiments.

2.4. ZIF series

ZIFs are a branch of metal-organic skeleton, and they are similar in structure, so this new zeolite imidazoline skeleton material was named ZIFs, with high thermal and chemical stability ^[17]. Zhang ^[18] et al. used zinc acetate dihydrate and 4,5-dichloro-1-hydroimidazole as raw materials to synthesize ZIF-71 for adsorption and separation of low-concentration bio-based 2,3-butanediol/1,3-propanediol. The adsorption principle of the experiment was revealed by molecular simulation. The experimental results show that ZIF-71 has a large specific surface area and a rich pore structure, which can provide a large number of adsorption sites and improve the adsorption efficiency. And in experiments with ZIF-71 undergoing three cycles of adsorption and desorption, ZIF-71 showed excellent stability and regeneration. Therefore, ZIFs materials are expected to become adsorbent for selective adsorption separation of low concentration by-products 2,3-butanediol, and promote the industrial development of biological system 1,3-prolene glycol.

3. Construction of the heterojunctions based on the MOFs

In terms of the photocatalytic degradation of single MOFs, their stability is poor and the active site is limited, so there is still a lot of room for improvement in the treatment of refractory organic matter. Generally, one of the main ways to improve the photocatalytic degradation performance of MOFs-derived materials is the integration of semiconductor or conductive materials into MOFs materials to improve the photocatalytic efficiency of catalyst degradation through adsorption-in situ degradation. MOFs are used as platforms to integrate the functional characteristics of different materials to enhance the utilization of light and promote the separation of photogenerated charge carriers to realize the occurrence of light-driven catalytic reactions.

3.1. Construct a heterojunction with the semiconductor TiO2

Li ^[19] et al. synthesized the TiO₂-Fe₃O₄ / MIL-101 (Cr) magnetic composite photocatalytic material by in situ hydrothermal method, and the addition of TiO₂ significantly broadened the visible light response range of the composite photocatalytic material. In the simulation experiment of photocatalytic degradation of methylene blue (MB), the degradation efficiency of TiO₂ was significantly enhanced than that of the addition, and when the amount of TiO₂ is 400 mg, the degradation efficiency of MB can reach 80%. The magnetic composite prepared has good stability in the degradation process, and due to the high specific surface area of the metal-organic skeleton material MIL-101 (Cr), pollutants can be enriched on the surface of the photocatalytic material and increase the interface concentration, so that the heterogeneous photocatalytic reaction can be significantly improved.



Figure 2. Mechanism of photocatalytic MB of TiO₂-Fe₃O₄ / MIL-101 (Cr)

Xue ^[20] et al. prepared a nanotube array of TiO₂ modified with the organic skeleton-MIL-125 and NH₂-MIL-125. prepared nanotube arrays of TiO₂ modified by the organic skeleton MIL-125 and NH₂-MIL-125. Through methylene blue degradation test, it was found that modified MIL-125 and NH₂-MIL-125 can improve the photocatalytic activity of TiO₂ nanotube array under ultraviolet light irradiation; however, NH₂-MIL-125 / TiO₂ nanotube array showed the highest photocatalytic performance in visible light and solar light. Ma ^[21] et al. prepared NH₂-MIL-125 (Ti) / TiO₂ composite nanofibers by electrospinning technology combined with solvent thermal method. The XRD characterization analysis shows that the loading of NH₂-MIL-125 (Ti) does not affect the crystalline phase of the TiO₂ nanofibers. The morphology of NH₂-MIL-125 (Ti) / TiO₂ composite nanofibers was observed by scanning electron microscopy, and small particles were evenly distributed on the nanofiber surface. The desulfurization performance of NH₂-MIL-125 (Ti) / TiO₂ composite nanofibers was studied in the extraction catalytic oxidation desulfurization system, and the results showed that the composite nanofibers have the potential of industrial desulfurization.

Hu ^[22] prepared TiO₂ nanosphere by hydrothermal method, and co-modified ZIF-67 and ZIF-8 on the nanosphere surface by sol gel method, and successfully prepared ternary heterojunction TiO₂ / ZIF-67 / ZIF-8 nanosphere. The results show that the synergistic interaction between ZIF-67 and ZIF-8 facilitates the transport of charge at the interface, accelerates the electronhole separation rate, and effectively improves the photocatalytic activity and photoelectric chemical properties of TiO₂. The synergistic interaction between ZIF-67 and ZIF-8, which facilitates the transport of charges at the interface, accelerates the electron-hole separation rate, and effectively improves the photocatalytic activity and photochemical properties of TiO_2 and MOF.

3.2. Construct a heterojunction with the semiconductor CN

Li ^[23] et al. loaded different proportion of FeMn-MOF on CN.Different masses of CN were added to the DMF solutions of FeCl₂·4H₂O and MnCl₂·4H₂O and sonicated for 60 min to uniformly disperse the metal ions over the CN with the same subsequent synthesis steps as FeMn-MOF. Dissolve H₂BDC in 30 mL DMF solution. After sufficient dissolution, the two solutions were mixed and sonicated for 30min to 100 mL stainless steel reactor with PFE lining. After static crystallization at 120 °C for 24h, after natural cooling, the products were washed with DMF and absolute ethanol and dried in a 60 °C vacuum oven. The properties of the product were investigated and showed that FeMn-MOF and CN bind well and had strong photocatalytic activity.

Energy shortage and environmental pollution problems increasingly serious, Chen $^{[24]}$ et al.explore the semiconductor photocatalytic materials to remove organic pollutants, with MIL-125 (Ti) as the photocatalyst carrier, g-C₃N₄ for organic semiconductor, Fe₃O₄@SiO₂ as the magnetic carrier, a series of visible mass ratio of ML-125 (Ti) composite materials. The sample composition, structure, morphology, and optical properties of the composite materials were characterized by Fourier transform infrared spectrometer, X-ray diffraction instrument (XRD), field emission scanning electron microscope, and thermal weight analyzer. The experimental results show that this composite is a good photocatalyst with excellent degradation properties of MB.

Peng ^[25] et al. prepared MIL-53 (Fe) / g-C₃N₄ composite material of MIL-53 (Fe) and g-C₃N₄ by solvent-thermal method, and characterized the structure, morphology, adsorption characteristics and photochemical characteristics by X-ray diffractometer and Fourier transform infrared spectroscopy (FT-IR). The results showed that g-C₃N₄ was stripped and granular, which increased the contact area with MIL-53 (Fe), allowing g-C₃N₄ to bind closely with MIL-53 (Fe). MIL-53 (Fe) / g-C₃N₄ composite has the best photocatalytic activity under visible light, and the photodegradation rate of RhB is 5 times higher than g-C₃N₄, which is attributed to the effective recombination and energy level matching of MIL-53 (Fe) and g-C₃N₄, which promotes the separation of photogenerated electron holes, while also increasing the specific surface area and improving the photocatalytic activity.

3.3. Construct a heterojunction with the semiconductor ZnO

Ma ^[26] et al.first prepared the ZnO base, and then obtained the continuous dense ZIF-67 membrane at the base through the hydrothermal reaction. Applied XRD to analyze the crystal structure. The ZIF-67 membrane matched the diffraction peaks of the ZIF-67 powder and the ZnO substrate, demonstrating successful ZIF-67 growth on the ZnO substrate. The membrane remained permeable and selective when the pressure was reduced from 5.0 bar to 1.0 bar.

Samy^[27] et al. successfully prepared MIL-53 (Al) / ZnO composite by high pressure reactor, and optimized the effect of operating parameters by response surface method on trimethoprim (RSM). It proved a good interaction between ZnO and MIL-53 (Al) and formed the consolidated nanoparticles. MIL-53 (Al) / ZnO was coated on the plate for a photocatalytic reaction to examine the effect of different pH values, initial concentration and flow rate on the degradation performance of trimethoprim.

Xiao ^[28] et al. prepared MIL125-ZnO by simple hydrothermal method in the presence of zincfree MOF such as MIL-125 (Ti). The experimental results showed that the photocatalytic activity of ZnO was improved compared with that of ZnO prepared without MOFs

4. Conclusion

This paper introduces the common MOFs materials and their derivative materials for constructing heterojunctions. With the progress of science and technology, the social requirements for MOFs materials are increasing, and the single MOFs have been difficult to meet the requirements of people in the field of catalysis and adsorption. The modification of MOFs with wider spectral response range, higher carrier separation efficiency and higher charge transmission rate has become a hot topic in this field.

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