Metal-Organic Frameworks for Photocatalytic Degradation of Organic Wastewater

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Abstract. Environmental problems, including garbage disposal, land desertification, water pollution, and sand disaster, especially water pollution, should be faced seriously by human beings. Photocatalysis technology has been increasingly playing a dominant role in treating organic wastewater. This paper will introduce the degradation of organic wastewater using metal-organic framework (MOF) materials photocatalytic technology. This paper will summarize the related articles and research results published by the previous generation. This paper will introduce the material characteristics of MOFs and the physical and chemical properties of the materials and then will present the advantages of MOF materials in the photocatalytic degradation of organic wastewater. The working principle of MOFs for photocatalytic degradation of organic wastewater and the method of making MOF materials will be introduced. At the end of the article, the results of previous research in this field in recent years will be presented.

Keywords: Metal-organic frameworks, photocatalysis, degradation of organic wastewater.

1. Introduction

With the progress and development of society and technology, the water demand in our daily life and industrial production has increased, and a large amount of organic wastewater is produced. As people are now paying more attention to environmental issues, the requirements for the quality of wastewater discharge are becoming more stringent, so the technology and methods for treating organic wastewater are particularly important. Photocatalytic technology can effectively degrade organic wastewater, and solar energy is a clean, non-polluting, and renewable green energy source. However, many materials have low photocatalytic efficiency and poor structural modulation, which limit their further application in photocatalysis. Therefore, developing new and efficient photocatalytic materials is of immense importance.

The discovery and development of metal-organic framework (MOF) materials offer hope for photocatalytic materials. These are an emerging class of three-dimensional porous materials with a periodic network structure formed by metal or metal-oxygen clusters linked by oxygen- or nitrogen-containing multi-dentate organic ligands. MOFs are characterized by high crystallinity, large specific surface area, high porosity, regular pore structure and a tunable composition structure, As shown in Figure 1 and Figure 2. The metal-oxygen units in their structures can be regarded as discrete semiconductor quantum dots connected by organic ligands, so MOFs also have semiconductor-like properties and are a promising class of photocatalytic materials.

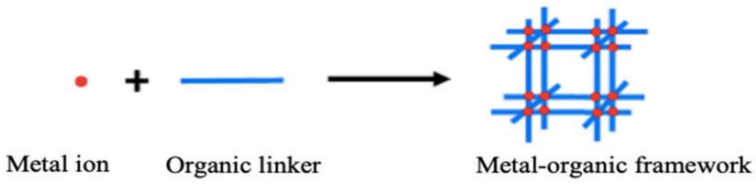

Figure 1. The schematic diagram for the formation of the MOF from metal ions and organic linkers as precursors. Reproduced with permission from Reference [1]

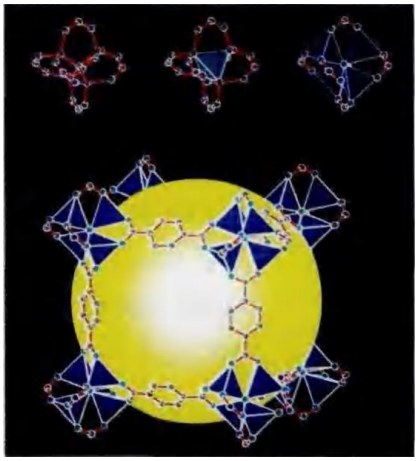

Figure 2. The construction of the MOFs-5 framework [2]. Zn_4O $(CO_2)_6$ cluster and 1,4-benzene dicarboxylate form a cubic structure. The middle yellow sphere represents the biggest van der Waals ball that that aperture can hold

This article summarizes the academic studies of many previous scholars and summarizes the research results of MOFs in photocatalytic degradation of organic wastewater. The following article will introduce the working principle of MOFs for photocatalytic organic wastewater and the advantages in this field, respectively. The synthesis methods of MOFs and the recent research results of scholars will also be introduced.

2. The principle working mechanism of photocatalytic degradation of organic wastewater

When irradiated by light, the organic linker in the MOF can function as an antenna for receiving light energy. Light energy from outside the system is received, and under excitation by light energy, photogenerated electrons and photogenerated holes are produced when the MOFs material absorbs photons with energy greater than the intrinsic forbidden bandwidth. The photogenerated electrons are transferred from the highest occupied molecular orbital (HOMO) of the MOF to the lowest unoccupied molecular orbital (LIMO) and then to the surface of the metal-oxygen cluster. The metal cluster nodes or organic ligands in MOFs can be the active sites for photocatalytic reactions. The metal cluster nodes or organic ligands in MOFs can be the active sites for photocatalytic reactions. Here, the photogenerated electrons and holes undergo their respective redox reactions with the reaction substrate. Oxygen molecules can trap photogenerated electrons (e^-) to form superoxide radicals ($-O_2^-$). Photogenerated holes (h^+) in the HOMO orbitals can not only oxidize organic molecules directly but also react with water molecules to form hydroxyl radicals (-OH) due to their powerful oxidizing power. The number of active sites in the MOFs has a crucial influence on the efficiency of the photocatalytic reaction and the concentration of the reacting substrate, as shown in Figure 3.

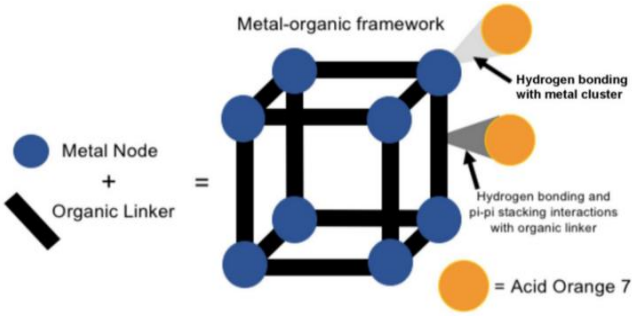

Figure 3. Interactions in adsorption of a contaminant (acid orange 7) onto the pores of MOFs. Reproduced with permission from Reference [3]

Hydroxyl radicals ($^{\cdot}OH$) and superoxide radicals ($-O_2^{-}$). Both reactive species are considered to have an extremely high oxidation capacity. The hydroxyl radical is the most oxidizing and reactive oxide species with strong electronegativity and a high oxidation electrode potential (2.8 V). It can react with most organic wastes in organic wastewater in diverse chemical reactions, including hydrogen abstraction, oxidative decomposition, electron transfer, and addition reactions. Superoxide radicals have unpaired electrons and are therefore very reactive and can be used as oxidants to oxidize and degrade organic pollutants in organic wastewater. They both adsorb into the organic pollutants in the wastewater and subsequently break all the chemical bonds in the pollutants, breaking down the waste into H_2O and CO_2 eventually. Both reactive substances can be generated by the absorption of light energy by the MOF.

Recently, Pan et al. synthesized two structures of MOFs: [(Cu(H_2L)) (4,4'-bipy)$_{0.5}$(H2O)] and [Co ($C_{14}H_{14}O_{6.5}P_2$) (4,4'-bipy)$_{0.5}$(H_2O)$_2$]·H_2O [4]. These two have the properties of reducing hexavalent chromium to trivalent chromium and degrading MB under UV illumination, and the reaction mechanism is proposed:

$$MOFs + hv \rightarrow MOFs(h^+ + e^-) \quad (1)$$

$$MB + h^+ \rightarrow CO_2 + H_2O + other \quad (2)$$

$$h^+ + H_2O \rightarrow OH^{\cdot} + H^+ \quad (3)$$

$$O_2 + e^- \rightarrow O_2^{\cdot -} \quad (4)$$

$$MB + OH^{\cdot} + O_2^{\cdot -} \rightarrow CO_2 + H_2O + other \quad (5)$$

MOFs materials can, in principle, contain a photosensitizer and a catalytic center in a single solid and provide a backbone structure that integrates all three. This is an especially important research value for the realization of artificial photosynthesis.

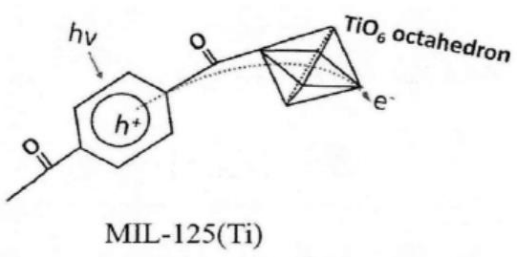

Figure 4. Schematic sketch of the charge transfer process of MOF MIL-125(Ti)

After illumination, the organic ligands of MOFs materials absorb light energy, and the electrons generated by excitation are transferred to metals or metal clusters through the charge transfer process of organic ligands. The photogenerated electrons are transferred, and the materials have photocatalytic activity. Take MIL-125 type MOFs as an example, the charge is generated in the benzene ring after being excited by light, and the electrons then migrate to Ti^{4+} in the titanium oxygen octahedra to undergo photocatalytic redox processes, such as the photocatalytic reductions of aquatic hydrogen and CO_2 in the presence of sacrificial agents [5].

Although MOFs show good potential as adsorbents and photocatalysts for pollutant remediation, some are plagued by poor chemical and moisture stability and the inability to harness solar energy. MOFs have been combined with other functional materials to overcome these drawbacks, such as metal and metal oxide nanoparticles. Wang et al. (2019) proposed the mechanism of enhanced photocatalytic degradation of rhodamine blue dye using CQDs supported on NH_2-MIL-125(Ti) as follows [6]:

$$CQDs/NH_2\_MIL\_125(Ti) + hv \rightarrow CQDs/NH2\_MIL\_125 + e^- + h^+ \quad (6)$$

$$e^- + O_2 \rightarrow O_2^{\cdot -} \quad (7)$$

$$O_2 + H_2O \rightarrow HO_2^{\cdot} + OH^{\cdot} \quad (8)$$

$$HO_2^{\cdot} + H_2O \rightarrow H_2O_2 + OH^{\cdot} \quad (9)$$

$$H_2O_2 \rightarrow 2\,OH^{\cdot} \quad (10)$$

$$h^+ + OH^- \rightarrow OH^{\cdot} \quad (11)$$

$$OH^{\cdot} + RhB(dye) \rightarrow CO_2 + H_2O \quad (12)$$

$$h^+ + RhB(dye) \rightarrow CO_2 + H_2O \quad (13)$$

3. The distinctive merits of MOFs

MOFs, formed by the self-assembly of metal ions or metal clusters with organic ligands, are a relatively new class of porous crystalline solid materials, which generally have the advantages of high porosity, high specific surface area, structural tailor ability, easy functionalization and multiple active sites, and have shown great promise in the fields of gas storage and separation, molecular sensing, optoelectronic materials, drug carriers and catalysis. Among the functional applications of MOFs, photocatalysis is one of the areas that has developed extremely rapidly in recent years, and a considerable variety of MOFs have also shown many semiconductor-like properties. The high porosity of MOFs contributes extensively to the photocatalytic process by trapping pollutants. A porous material like MOF has particularly good prospects in photocatalysis. Its porous structure allows for the exposure of as many reactive sites as possible while at the same time reducing diffusion resistance to facilitate contact between the reactive substrate and the active site. The rich internal surface area of the porous structure allows for a much shorter transport distance between the photoelectrons and holes, which to a certain extent avoids the complexation of the bulk phase in the photocatalytic process, thus increasing the efficiency of the separation and utilization of photoelectrons and holes and greatly improving the photocatalytic performance. MOFs are also highly designable and can be modified or combined with other compounds to improve the efficiency of photogenerated electron-hole generation and separation. By introducing long-wavelength absorbing groups into MOFs as organic bridging ligands (e.g., amino groups, metal complexes, porphyrins, etc.) [7-14]. MOFs can enhance their light absorption, enabling visible and even near-infrared photocatalysis of MOFs and increasing the number of electron-hole pairs produced under solar illumination. MOFs containing Fe, Cr, Zr and Ti metal ions exhibit good stability in water and can collect and direct solar energy. They usually have a small band gap and can excite visible light [15, 16]; therefore, they are considered good candidates for the photocatalytic degradation of organic pollutants. In addition to the catalytic sites possessed by MOFs themselves, other active species can be embedded in the pore channels of MOFs. Combining the catalytic properties of these catalytic species with the unique topology of MOFs can lead to efficient and stable catalytic processes. Homogeneous metal-organic complexes usually have high catalytic performance, but the problems of difficult catalyst recovery and poor stability limit their further application. The use of the three-dimensional topology of MOFs is one of the effective ways to realize the recovery and recycling of homogeneous catalysts. In addition, the framework structure of MOF s can stabilize the active component and prevent catalyst deactivation.

Due to the functionality of organic linkers, MOFs also provide selective adsorption of organic molecules, forming inclusion complexes with the guest adsorbate molecules. The mode of adsorption interactions is usually through covalent bonds, hydrogen bonds, bonds with lattice, van der Waals forces and π-π interactions. Molecular simulations have shown that the guest molecule is preferably located in the pore of the MOF when the pore size of the MOF is larger than that of the contaminant molecule. Alternatively, if the guest molecule is larger than the pores of the MOF, it will adsorb on the outside. Therefore, selecting MOFs for the adsorption of analytes is important to optimize adsorption. MOFs with good adsorption properties have been used selectively to remove contaminants from water. Their stability, adsorption capacity and easy reusability have been reported.

4. Synthesis strategies of MOFs for photocatalytic degradation of organic wastewater

Recently, metal-organic backbone (MOF) has been heavily investigated as a class of hybrid inorganic-organic materials. Formally, MOF materials are ligand networks consisting of metal nodes and organic ligands. While the metals employed are ions or clusters, the metal nodes can be considered primary building units (PBUs) or secondary building units (SBUs). In addition, organic ligands are introduced as hybrid materials for the pillars of the building frame. This structure of MOFs can be described and organized by their subunits or topological networks. By repeating PBUs or SBUs using bridging ligands (e.g., carboxylic acid or carboxylate residues), these compounds can be further coordinated with other entities to form SBUs, tertiary building units (TBUs), or one-, two- or three-dimensional extensions to build MOF architectures. Details of the networks are available in the Reticular Chemical Structure Resource (RCSR). The properties of MOFs have been intensively studied due to the variety of selective metal centers and organic ligands used as building blocks, the different structures and, therefore, the nature of MOFs.

Typically, MOFs are synthesized by various approaches such as solvothermal, hydrothermal, microwave-assisted, acoustic, mechanochemical and electrochemical methods. Most of these methods are conducted in the liquid phase. With the addition of a solvent, metal salts and organic ligands can be more easily mixed and assembled to obtain organized structures and crystallization. Therefore, a suitable solvent must be selected to determine the synthesis environment, including reactivity, solubility, redox potential and stability constants.

4.1. Solvothermal and hydrothermal methods

The solvothermal method is the most widely used technique for synthesizing MOFs due to its convenience, ease of operation and high productivity [17]. First, the metal-centered precursors and organic ligands are dissolved or mixed in an organic solvent. The metal center and organic ligand precursors are poured with the solvent into a closed vessel, either a glass vial for low-temperature reactions or a Teflon-lined stainless-steel autoclave for elevated temperatures (>400 K). Subsequently, the closed vessel is heated above the solvent's boiling point to generate higher pressures. The synergistic effect of solvent, temperature and pressure allows precursors (both insoluble and insoluble) to start participating in the synthesis reaction, leading to the enhanced assembly of the MOF structure.

4.2. Microwave-assisted, acoustic chemistry

As solvent-thermal and hydrothermal methods rely on thermal energy to induce crystal formation and growth, microwave-assisted, acoustic-chemical, and electrochemical methods use microwave radiation, ultrasonic radiation, and electrical energy to assist or accelerate the synthesis of MOFs [18-20]. For example, microwave-assisted methods allow the rapid synthesis of MOFs with production quality like those prepared by conventional synthesis methods without microwave assistance. Microwaves can replace the heat source to heat the mixed solution with better efficiency, thus reducing the synthesis time.

As for the sonochemical methods, ultrasonic radiation facilitates chemical or physical reactions. When ultrasonic radiation is applied, cavitation bubbles will form and implode in the mixed solution due to pressure changes at high frequencies (20 kHz to 10 MHz). The collapsed cavities will generate strong shock waves, leading to the creation of local hot temperatures and pressure hot spots. These hot spots can facilitate the chemical synthesis of MOF to form crystalline nuclei.

4.3. Solvent-free methods

To reduce the use of chemical solvents, the solvent-free synthesis of MOF is a simple, environmentally friendly, and economical process [21, 22]. For example, mechanochemical methods are solvent-free synthesis that uses mechanical energy to conduct the synthetic reaction. Initially, the metal center and the organic ligand precursor are placed in a steel bowl, and then two or three ball

mills grind the powder mixture at a low frequency (25 Hz). Next, a small amount of solvent (1 mL) is added, and further grinding is carried out at a higher frequency (40 Hz). While observing the change in color of the powder, the samples were dried in the air, stirred in ethanol or ethanol and water solvent, filtered and then washed with ethanol. Ultimately, MOF was obtained as a preparation sample.

5. Recent progress of MOFs in photocatalytic degradation of organic wastewater

Photocatalysis is a very practical application technology initiated to solve the two major problems of energy shortage and environmental pollution. The MOFs material has a high specific surface area, high porosity, adjustable structure function, and excellent photophysical and photochemical properties and semiconductor characteristics. Photocatalytic technology can have great practical application value in degrading organic wastewater, so increased researchers pay attention. Generally, materials with high porosity, high specific surface area and electron conduction properties are rare. However, MOFs materials have high porosity and tunable electron conduction properties simultaneously, which opens a series of new applications for these materials. This is of great research value for the realization of artificial photosynthesis.

In the past decade or so, increased MOFs materials have been applied to the field of photocatalysis. In principle, MOFs can contain a photosensitizer and a catalytic center in a single solid and provide a backbone structure that simultaneously possesses the three necessary components for artificially simulated photosynthesis. Since the late 1990s and early 2000s, MOFs have been considered a potential photocatalyst. Early studies on the photocatalytic aspects of MOFs were based on MOFs' similarity to inorganic semiconductors, except those MOFs structures are composed of bridging organic ligands and metal linkages. Many MOF materials exhibit a wider UV-visible absorption range than conventional semiconductors. 2007, the photocatalytic degradation of phenol by M0F-5 solution was the first report on the application of MOFs in photocatalysis. Subsequently, MOFs materials have been applied to various applications such as photocatalytic degradation of organic dyes, photocatalytic decomposition of water, and photocatalytic reduction of C02.

The stability of the MOFs framework to water depends on the bonding strength of the metal nodes to the organic chains. The bonding strength of O or N is determined by the P& of the organic chain and the Lewis acidity of the ligand metal. Taking the decomposition of water as an example, MOFs materials need to maintain certain stability in an aqueous environment as well as withstand some other factors, such as pH, water redox sacrificial agents, sensitizers, solvent polarity and solvation of metal ions, which can affect the stability of MOFs frameworks. Furthermore, the photocatalytic efficiency of most MOFs materials is low, so it is necessary to explore efficient MOFs photocatalysts and find means to improve their photocatalytic efficiency to meet the needs of practical applications.

Wastewater is a key part of the water cycle, and a substantial portion of the world's wastewater is currently uncollected and untreated. Releasing wastewater that has not been treated must be very harmful to the environment and human health. In turn, a considerable proportion of wastewater is organic pollutants. Therefore, many scholars have studied the subject of photocatalytic degradation of organic wastewater by MOFs, and the number of publications related to this subject has been increasing year by year in the past 20 years since 2000, reflecting the continuous increase of research and attention in the field of photocatalysis, among which, the scientific enthusiasm of China in the field of photocatalysis is much higher than that of other countries and regions. In December 2017, Prof. Chongchen Wang's team from the Beijing University of Architecture published a research paper in the Chinese Journal of Catalysis (2021 Impact Factor: 8.271), a journal in the field of environmental engineering, on a stable two-dimensional coordination polymer for photocatalytic reduction of Cr(VI) and degradation of organic dyes [23]. In January 2019, the authoritative journal in the field of environmental engineering, Chemical Engineering Journal (2021 Impact Factor: 13.273), published a research paper by Prof. Chongchen Wang's team at the Beijing University of Architecture on the efficient photocatalytic reduction of Cr (VI) by UiO-66-NH_2(Zr/Hf) metal-organic skeleton films

under solar irradiation. In the paper, a detailed description and analysis of the related work are presented, and the mechanism of the photocatalytic reduction of Cr(VI) by UiO-66-NH_2(Zr/Hf) thin film, the influence of a range of factors on its photocatalytic performance, the future challenges and new ways for efficient photocatalytic removal of pollutants from wastewater by MOFs membrane photocatalysts are discussed.

6. Conclusion

Metal-organic skeletal materials are solid-state molecular structures constructed by linking organic ligands with metals or metal clusters and have become a class of solid catalysts with diverse functions and constructible active centers. MOFs catalysts are easily separated from the reactants for reuse, their molecules are chemically diverse and adjustable for various catalytic reactions, and they have made satisfactory progress in photocatalysis. At the intersection of the MOFs and the reaction medium, the chemical energy generated by the redox reaction can be transferred by electrons or reacted with the active species diffused into the pore channel of the MOFs. Photocatalysis can use solar energy to oxidize and decompose organic pollutants in water and converts solar energy into chemical energy with high energy density, easy transportation and storage, and suitable for application under extreme conditions. Photocatalytic decomposition of organic wastewater has important scientific research significance and practical application value because of its ability to produce clean, non-polluting, and abundant hydrogen energy. In recent decades, to solve the social problem of an energy shortage, photocatalytic water decomposition technology research has received wide attention from scientists at home and abroad. MOFs materials have excellent research value in the photolysis of water due to their unique structural and functional tunability, large specific surface area and high porosity.

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