Structure and application of flexible MOFs materials

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Abstract. The research on MOFs materials is currently a hot topic in the academic community. From the existing research results, it can be seen that the structure and composition of MOFs materials have been thoroughly studied. However, the relevant research on the application and research prospects of MOFs materials, especially MOFs flexible materials, is still not perfect. Based on the above research motivation, the research content of this article focuses on the structure and application prospects of flexible MOFs materials, and mainly draws the conclusion that they have enormous development potential and attractive development prospects in modern material research.

Keywords: MOFs flexible materials, organometallic skeleton compounds, development research.

1. Introduction

MOFs is the abbreviation of Metal Organic Framework compounds (Metal Organic Framework). It is a kind of crystalline porous material with periodic network structure formed by the inorganic metal center (metal ion or metal cluster) and the organic ligands connected by self-assembly. MOFs is a kind of organic-inorganic hybrid materials, also known as coordination polymers, which is different from inorganic porous materials as well as general organic complexes. It has the rigidity of inorganic materials and the flexibility of organic materials. Make it in the modern material research has presented a huge development potential and attractive development prospect.

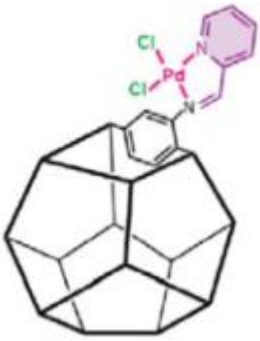

Figure 1. MOFs structure diagram under the insertion mechanism.

Eighty years ago, few people in the world had heard of plastic. But in 1939, one of the plastics - nylon - became a household name almost a year after its debut at the New York World Expo. Although nylon was popular in the stockings market for a while, the popularization of plastic in fields such as clothing, kitchenware, electronic products, building materials, and medicine has been going on for decades. Nowadays, we know that plastic has indeed become the material defining the 20th century. Since Yaghi founded MOFs materials in 1999, MOFs materials have been a hot research topic for scientists in various countries. As shown in the figure below, the number of journal publications on MOFs materials has also rapidly increased between 2005 and 2019.

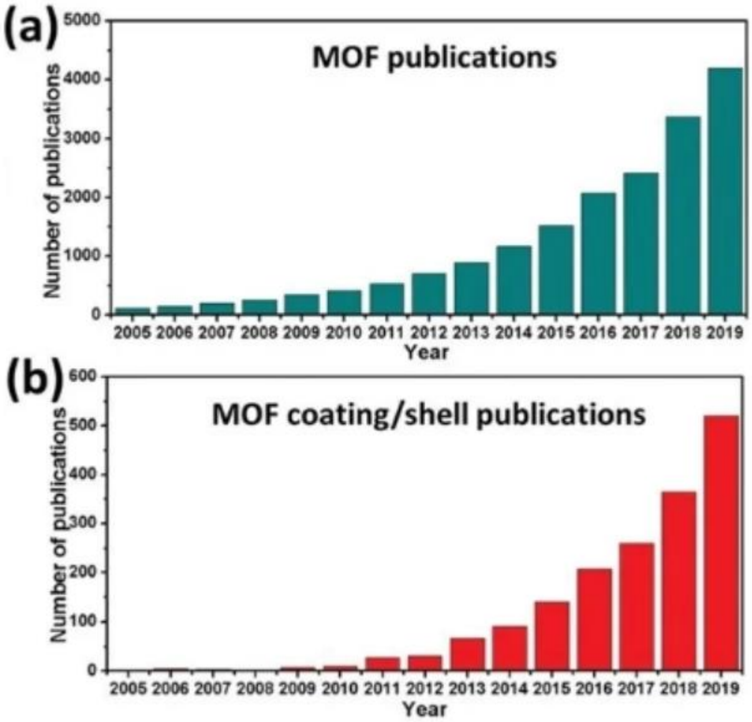

Figure 2. Data from the number of publications related to MOFs and MOF coatings in the American Journal of Chemistry [1].

In the future, metal organic skeleton materials (MOFs) are expected to become decisive materials in the 21st century. Although research on this group of three-dimensional nanocrystalline structures is still in its early stages, its commercialization projects are rapidly underway. You may never have heard of MOFs, but in 50 years, we believe they will become an indelible part of human life, just like plastic today. Transmission Electron Microscope (TEM) is a high resolution, high magnification electron optics instrument that uses an extremely short wavelength electron beam as the illumination source and uses an electromagnetic lens to focus and image. The accelerated and concentrated electron beam is transmitted to a very thin sample, and the electron collides with the atoms in the sample to change the direction, resulting in solid angle scattering. The size of the scattering angle is related to the density, thickness, and other factors of the sample, so it can form images with different shades. The images are displayed on imaging devices (such as fluorescent screens, films, and photosensitive coupling components) after amplification and focusing.

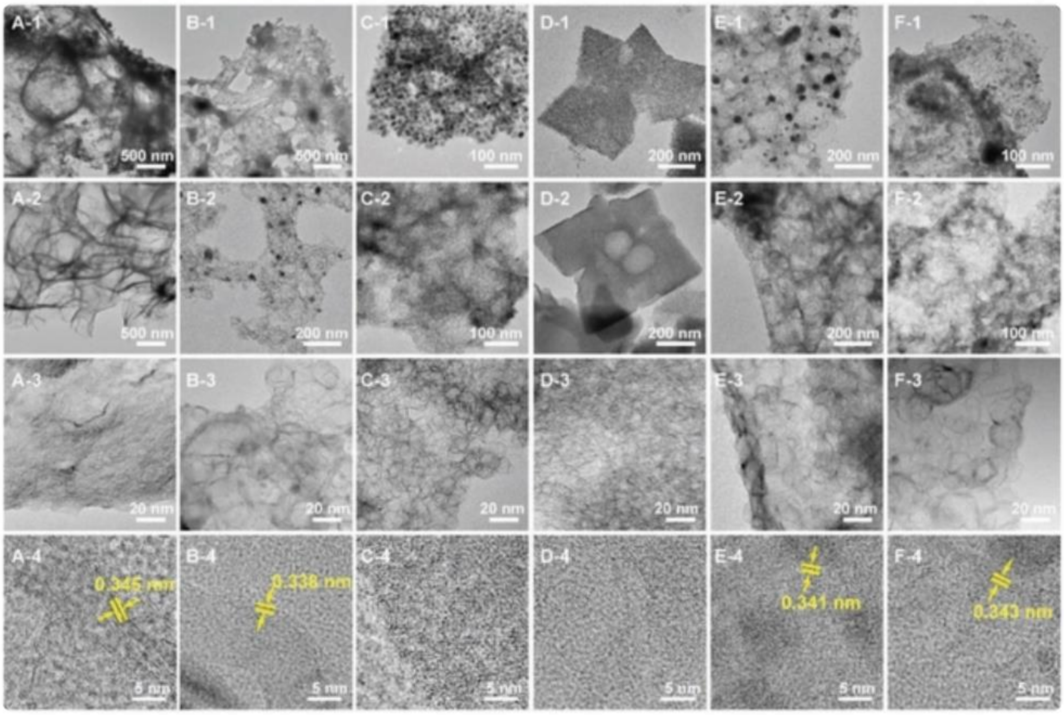

Figure 3. Data related to the transmission electron microscope morphology table from "Medicines and Nutrients in Continent Europe" [2].

The reason why plastic has become so popular in society is due to its versatility. Plastic, as a polymer, is a long and repetitive chain of monomers, which gives them different characteristics. By simply changing the monomer, the size, hardness, elasticity, transparency, and even conductivity of the polymer can be changed.

Like polymers, MOFs are multifunctional materials that consist of small, repetitive units. In this case, this structure is a nanoscale metal cluster connected by organic molecules. Unlike polymers that grow only in one direction, MOF materials can form crystals in all directions. They have a very rigid, uniform, and precise atomic arrangement·[2].

This unique uniformity enables scientists to design and process MOFs with unprecedented precision. By accurately understanding the position of each atom in the MOF, computational tools can quickly establish models to simulate different possible structures before synthesis in the laboratory. Although MOF's current applications are relatively niche, such as stabilizing toxic gases in the manufacturing process of electronic products such as silicon chips in smartphones, we believe they are at a tipping point, just like plastic 80 years ago.

2. Application of flexible composite material in structural expansion joint plugging

MOF is a crystalline material with a periodic network structure formed by self-assembly of organic ligands containing oxygen or nitrogen and transition metals. It generally has the structure of zeolite and zeolite like structures. In today's society, MOFs have received attention from multiple disciplines due to their structural and pore design, tailorability, and large and porous surface area. MOF can be applied in absorption, gas storage, sensor design, light harvesting, biological development, drug delivery, and catalysis·[3].

The nano MOF materials obtained now have completely different properties from ordinary solid materials, such as interference and scattering optical properties due to their small size. For example, they exhibit longer plasma circulation times in biology, and some can even be transported in the lymph.

The morphology of MOF materials is also crucial. The spherical shape ensures consistent ablation speed and can therefore serve as a drug corrosion inhibitor. Instead of being spherical or anisotropic due to their catalytic activity at the edges and corners, MOF membranes or thin sheets are crucial for gas separation and detection. That is to say, the size and shape of MOFs determine their functionality [4]. For zero dimensional nanostructured crystals, the author introduces the methods of sonochemistry and microwave assisted synthesis, whose principle is to generate hot spots (instantaneous high temperature, high pressure, and extremely fast heating and cooling rate), so that the nanocrystals can be cooled down in one thousandth of a second. In contrast, microwave assisted methods are superior to conventional and ultrasonic methods because they are not affected by reactant concentration and have higher yields compared to ultrasonic methods. Next is emulsion synthesis, which often requires supercritical fluids (conditions are too harsh). Finally, the interface synthesis was introduced, and the process of preparing crystals using T-junction was mainly introduced. The droplet containing metal in the aqueous phase and the organic phase containing coordination groups immediately contacted to form extremely small latex particles, thus obtaining MOF capsules. Because the concentration of solvent, MOF precursor, and contact rate can be adjusted, the diversity of control methods can be achieved, increasing the scope of use of this method. For one-dimensional nanostructured crystals, the author first introduces the reverse microemulsion synthesis method assisted by surfactants. As mentioned earlier, the size and shape of micelles can be controlled by adjusting the ratio of water phase to surfactant w. However, a change in w will only cause a change in particle size, without affecting the aspect ratio. In addition, due to the stabilizing effect of surfactants, higher concentrations of crystals can be obtained. If the metal has magnetism, it can be used for nuclear magnetic resonance imaging. Then, the interface synthesis in a relatively new microfluidic environment was introduced, using the "Lab on Chip" technology [5]. The principle is that the water phase containing coordination groups and the water phase containing metals undergo surface contact during the flow process. Through X-ray diffraction technology, it was found that linear nanocrystals formed during the microsecond period, and electron microscopy scanning showed that neatly arranged linear nanocrystals were obtained. However, although this method is simple, its molecular size distribution is too large, so it has not yet been widely applied. Then we will introduce the use of modulators for regulation as mentioned above. Because modulators are connectors of unit points, they can prevent crystal growth in a certain direction, leading to shape changes. For example, under a projection electron microscope, it was found that with time, crystals added modulators (such as acetic acid) grow in a certain direction without changing in diameter [6].

Growth templates mainly use modified graphene nanolayers as nucleation sites for crystals, while on graphene, hydroxyl or carboxyl groups are generally modified. The reactants react with hydroxyl or carboxyl groups to grow and self-assemble on graphene plates. Coincidentally, the example given in the article shows that the crystal growth direction is exactly the same as the exposed surface of graphene, and the radius of the graphene layer is the same as the obtained linear nanomaterial. These coincidences all lead to good growth of linear crystals. For two-dimensional crystals, the author mainly introduces the deposition of MOF colloids, gel layer approach, layer by layer growth, and top down fabrication. The colloidal particle sedimentation method uses the sedimentation of colloidal particle suspension, whose size is bimodal distribution (structural voids and lattice voids) [7]. This kind of regular micropores and mesopores has a considerable application market. Firstly, it rapidly diffuses into the mesopores and then enters the micropores. The membrane prepared by this method has been applied as a catalyst or gas sensor. However, the disadvantage is that the crystal made by it has no directionality, while the gel layer method has directionality. It uses a modified substrate as a template. It can adjust its growth range and thickness through the concentration of metal on the gel layer. Then the author described the layer by layer stacking method, which mainly involves obtaining a substrate with functional group modifications (mostly hydroxyl and carboxyl groups), and then periodically wetting and washing the substrate in a solution of metal ions and organic ligands to obtain MOFs. This method can accurately control thickness and direction. However, the disadvantage is that the substrate needs to be pre-treated to obtain the required functional groups. Cutting method is a recently researched method. Some scholars use ultrasonic wave to peel off the obtained MOF crystal, and then conduct photographic analysis through atomic force microscope (AFM). It was found that the monolayer can be peeled off, and the results are in good agreement with theory. But currently under research, the remaining relevant information is still incomplete. Not only can the shape determine the function of MOFs, but changing the constituent elements of MOFs or introducing other elements can also improve their function. The most mainstream now is post synthesis modification (PSM) and surface modification. PSM involves modifying the connecting molecules (with functional groups) on the original framework. Because PSM has been explored for many years, and the PSM of nano MOFs has received little attention, the author focuses on the surface modification of nano MOFs. Firstly, we talked about the shell structure. The half-life of drugs in the body can be prolonged by drug modification of nanoparticles and installation of shells (such as 2-9-nanometer silicon shells). Due to the certain cytotoxicity of drugs, targeted drug release can be achieved by changing the thickness of the shell and regulating the release rate of metals and organic compounds. Then the author introduced the heteroepitaxy of MOF on MOF. This method is more advanced than the previous method because it involves the interface interaction between the shell and core. By growing another MOF crystal shell on top of one MOF crystal, it has been proven to have different structural forms and surface pores. If the outer hole is small and the inner hole is large, it can be used to store gas of a specific size. This method creates performance with different properties on a single crystal without sacrificing the shape of the core crystal, nor reducing the original high surface area and pore volume [8].

3. Research progress on the application of MOFs materials in photocatalytic degradation of residual drug molecules in water

In recent years, with the rapid development of society, the number and types of new pollutants have also increased day by day. The serious water pollution problem has attracted close attention from researchers. The unreasonable discharge of industrial waste, the accumulation of traditional pesticides, and the unreasonable treatment of drugs are all causes of water pollution problems. These drugs have high toxicity and good chemical stability, which will directly or indirectly harm aquatic organisms, even the living environment of humans and animals. The pollutants accumulated in the soil will eventually enter humans and animals through various channels, posing a serious threat to their lives and health.

The chemical pollutants remaining in water are mainly divided into two categories: drugs and personal care products. Excrement, waste gas drugs, and directly discharged wastewater are all direct causes of serious chemical pollution in the water environment. The key to solving these problems lies in timely and reasonable treatment of harmful pollutants. Below is a brief overview of the ways in which different MOFs materials have been used to treat residual drug molecules in water in recent years.

3.1. Several treatment methods for residual drug molecules in water

At present, the main degradation methods for residual drugs in water include ozone or chlorine oxidation or traditional oxidation, but these methods have low oxidation ability and high selectivity. The most important thing is that toxic chlorinated products are produced during the chlorine oxidation process. The principle of oxidation is also adopted. Advanced oxidation has better effect. Advanced oxidation process mainly includes Fenton oxidation, O3/H2O2, UVA/H2O2, UVA/TiO2, photocatalytic oxidation, etc. The oxidation capacity of hydroxyl radical [OH] is also strong. Membrane treatment is a novel water treatment method, such as nanofiltration (NF), reverse osmosis (RO), microfiltration (MF), and ultrafiltration (UF). However, the inconvenient aspect of this method is that different membranes have different retention effects on different drugs. There are also methods of using activated carbon adsorption, among which the most commonly used are powdered activated carbon (PAC) and granular activated carbon (GAC), which have a good adsorption effect on general hydrophobic drugs. Ultrasonic decomposition is also used for the decomposition treatment of drugs in water, and its mechanism of action includes ultrasonic mechanical effect, thermal cracking effect, and free radical effect. Mendez [9] used 300kHz ultrasound to treat the refractory drug ibuprofen, with a removal rate of nearly 98% within 30 minutes.

3.2. Treatment of residual drug molecules in water using MOFs materials

MOFs material is a new type of porous material with good application prospects in photocatalytic degradation of organic compounds. The mechanism of MOFs degradation of drug molecules is that under light excitation, organic ligands can act as photosensitizers to generate electron hole pairs, thereby achieving charge separation and transferring to the central metal node. Equivalent oxidation and reduction reactions occur at the metal center of photocatalysis. MOFs materials with catalytic performance include pure MOFs materials and hybrid MOFs composite catalytic materials. By adjusting the optical properties of organic ligands and modifying the spatial configuration of secondary units, MOFs photocatalysts can improve the catalytic degradation efficiency of organic pollutants.

3.3. Catalytic degradation of drug molecules using pure MOFs materials

The research shows that the decomposition efficiency of pure MOFs materials for drugs may be related to the structure of central ions and coordination materials. Therefore, the improvement of pure MOFs materials mainly lies in exposing the active center metal, obtaining more photocatalytic active site, and improving the catalytic efficiency.

After activation, there are more metal center active site, and the degradation efficiency has also been improved, which has been shown in the degradation of drug molecule methylene blue (a drug used in aquaculture): Xing Yongyong's research group used 2,6-bis (2-benzimidazole) pyridine (L_1), 2,6-bis (5-phenyl-1H-3-pyrazole) - pyridine (L_2) as organic ligands with cobalt nitrate The reaction of nickel chloride and nickel acetate synthesized $[Ni_3 (H_2L_2)$ 2 · $(HL_2)_2]$ · (OH) 3 · (Ac)·

H_2O [10], $[Ni (HL_1)_2]$ and $[Co (HL_1)_2]$ have studied the effect of central metal on photocatalytic degradation. The results show that the activity of 2 with different central metal but similar structure is significantly higher than that of 3. 2 and 1 have the same central metal, but the secondary unit of 2 is a compound of mononuclear nickel double ligand, while the secondary unit of 1 is a compound of trinuclear nickel four ligand. The increased active site of the metal center after activation improves the degradation efficiency [10].

3.4. MOFs composite materials for photocatalytic degradation of drug molecules

While pure MOFs materials are applied to the degradation of drug molecules, some experimental results indicate that composite materials synthesized through hybridization based on MOFs often have good degradation effects as photocatalysts. For example, after TiO_2 is hybridized, the generated hydroxyl radical has strong oxidation ability under photocatalysis.

The rapid generation and effective separation of photo generated electron hole pairs are also crucial parts of the degradation of drug molecules in the process of producing electron hole pairs. The effective separation of photogenerated electrons and holes is also the most critical step in improving the photocatalytic efficiency. Therefore, in order to inhibit the recombination of electrons and holes and improve the photocatalytic efficiency, hydrogen peroxide (H_2O_2), potassium bromate ($KBrO_3$), sodium persulfate ($Na_2S_2O_8$), etc. are commonly used as electron acceptor [11].

For example, for drugs containing phenolic structures, the Pichiah Saravanan research group [12] has developed a novel structure, which includes Cd-MOFs with [Cd (btec) 0.5 (bimb) 0.5] n (bimb=4,4 '- bis (1-imidazolyl) biphenyl, H4btec=1,2,4,5-phenylenetetracarboxylic acid). The MOFs framework includes Fe3+that can enhance the excitation light response in the visible light region, as well as Ag+and Zn2+that can enhance the excitation light response in the ultraviolet light region, This structure can separate holes (h+) and photo generated electrons (e -), enhancing the activity of photocatalysts.

For antibiotics such as tetracycline (TC), Yuan et al. [13] synthesized a new core-shell type of drug In2S3@MIL-125 (Ti) (MLS) photocatalyst, which better opens the porous structure, enables more effective transfer of photogenerated carriers, transfers valence electron between Ti3+and Ti4+, as well as the role between MIL-125 (Ti) and In2S3. Its photocatalytic performance has been greatly improved compared with pure MIL-125 (Ti) and pure In2S3, and the photodegradation rate has reached 63.3%.

The application of nanocomposites based on MOFs has shown significant progress compared to traditional MOFs materials, but their manufacturing methods are relatively cumbersome. Wu et al. [14]

provided a simpler strategy for manufacturing nanocomposites. Wu et al. obtained a simple alcohol reduction method by doping Pd in MIL-100 (Fe) Pd@MIL-100 (Fe) also has high activity in the degradation of drug molecules,

In composite materials, TiO_2 is also a very practical material. Pure TiO_2 can only catalyze under ultraviolet light irradiation, which limits its practicality. Through research, it has been found that doping TiO_2 with other compounds or various carriers after composite modification increases the wavelength range of TiO_2 absorption light. However, after TiO_2 is hybridized, the hydroxyl radical that can be generated under photocatalysis has strong oxidation, and can degrade the drugs in the environment. In recent years, many modified TiO_2 have been widely used in the photocatalytic degradation of environmental drugs.

Luo Lisha et al. [15] prepared Ag-TiO_2 by the sol gel method. Under the condition of light, by studying the degradation effect of Ag-TiO_2 on tetracycline hydrochloride, they found that its degradation efficiency could reach 92%, which indicates that TiO_2 doped with Ag can efficiently degrade antibiotics in wastewater. Yao Wenhua et alsynthesized Co doped TiO_2 photocatalysts using hydrothermal method, which were used for the catalytic degradation of four pesticides: trichlorfon, omethoate, acephate, and dichlorvos, and also achieved good degradation results.

Li Lingdan et al. [16] prepared MOFs composite materials doped with multiple elements, and synthesized Fe and F co doped TiO2 photocatalysts using hydrothermal method under visible light. The degradation of bromate, a carcinogenic drug, was carried out, and the test results showed that after 60 minutes of degradation, the catalyst's degradation rate of bromate reached 100%

4. There are issues with MOFs materials

However, when MOFs materials are put into use, there are still some problems: the synthesis difficulty is higher than traditional adsorption materials, and the funding is too large; Low yield; Some MOFs materials are more sensitive to water. Currently, the main method used is to modify MOFs materials to enhance their degradation of target molecules.

5. Conclusion and outlook

MOFs and their composite materials are widely used for the photocatalytic degradation of harmful drugs, but the types of stable and practical MOFs and their composite materials are still limited. In the future, we can focus on purposeful regulation of MOFs and their composite materials, or targeted regulation and modification of a certain drug molecule. The practical application of MOFs and their composite materials in photocatalytic treatment of harmful drug molecules in wastewater still needs continuous exploration and research.

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