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SYNTHESIS OF TWO-DIMENSIONAL ORGANIC FRAME MATERIALS: CLASSIFICATION, APPLICATIONS, PROBLEMS AND MODIFICATION APPROACHES

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Abstract: Organic framework materials, including MOFs and HOFs, are widely used in multiple fields. MOFs are formed by the self-assembly of inorganic metal centers and organic ligands, and there are various types such as IRMOFs and ZIFs. Post-synthetic modification (PSM) can expand their functional groups. HOFs connect building units through hydrogen bonds. They have advantages like mild preparation conditions and good solution-processing performance, but the characteristics of hydrogen bonds also limit their development. Two-dimensional MOFs combine the advantages of MOFs and ultrathin two-dimensional materials. There are two preparation strategies: "top-down" and "bottom - up". The "top-down" method, including physical and chemical exfoliation methods, can exfoliate bulk MOFs into nanosheets, but there are problems such as uneven product thickness and low yield. The "bottom-up" methods, such as the solvothermal method, interface synthesis method, and auxiliary synthesis method, can prepare nanosheets with uniform thickness, but each has its pros and cons. Overall, organic framework materials have broad prospects, but they still face challenges in synthesis, performance optimization, etc., and further research and improvement are needed.
Keywords: Organic framework materials; MOFs; HOFs; Synthesis methods; Two-dimensional MOFs

1 OVERVIEW OF ORGANIC FRAMEWORK MATERIALS

1.1 Overview of MOFs

Organic framework materials mainly include MOFs (Metal-organic frameworks) and HOFs (Porous hydrogen-bonded organic frameworks). MOFs were first proposed by Yaghi, Li and others in the 1990s. It is a two-dimensional coordination compound synthesized from the rigid organic ligand trimesic acid (BTC) and the transition metal Co, and was named as MOF[1]. MOFs is the abbreviation of Metal organic framework. It is a kind of crystalline porous material with a periodic network structure formed by the self-assembly and connection of inorganic metal centers (metal ions or metal clusters) and bridging organic ligands[2]. MOFs are organic-inorganic hybrid materials, also known as coordination polymers. They are different from both inorganic porous materials and general organic complexes, and possess both the rigidity of inorganic materials and the flexibility of organic materials, showing great development potential and remarkable development prospects in modern material research.

At the beginning of the synthesis of MOFs, their porosity and chemical stability were not high. Therefore, scientists began to study coordination polymers formed by new types of cations, anions and neutral ligands. Currently, a large number of metal-organic framework materials have been synthesized, and carboxylic organic anions are the main ligands.

Generally, MOFs are composed of two parts, namely organic ligands and metal centers, which act as struts and nodes respectively. Therefore, according to the different component units and synthesis methods, MOFs materials can be divided into four categories:

(1) Isoreticular metal-organic frameworks (IRMOFs). IRMOFs are mainly formed by the bonding of [Zn4O6]+ metal clusters and carboxylic acid-based organic ligands to form a repeated network topological structure. IRMOFs have large cavities and pore volumes. Among the IRMOFs series, the most typical one is MOF-5[1].

(2) Zeolitic imidazolate frameworks (ZIFs). ZIFs materials are self-assembled by the coordination of Zn or Co with N on the dimethylimidazole (or imidazole derivative) ring. ZIFs have a series of advantages: easy functionalization, adjustable size and morphology, and good thermal and chemical stability. Among ZIFs, the most common and synthesized ones are ZIF-8[2] and ZIF-67[3].

(3) Metarial sofistitute lavoisier frameworks (MILs). MILs materials are materials formed by the coordination of trivalent transition metal ions (such as Fe, Al and Cr) or lanthanide metals with carboxylic acid-based ligands (glutaric acid, terephthalic acid, succinic acid, trimesic acid, etc.) through the hydrothermal method. MILs have extremely high specific surface areas. Among MILs, MIL-5[4] and MIL-101[5] are two common types.

(4) Ocket-channel frameworks (PCNs). Different types of MOFs materials can be transformed into each other by changing the structure or one of the elements, and they contain both a pore cage structure and a three-dimensional orthogonal pore channel structure. Compared with IRMOFs, the structure of PCNs is more complex. HKUST-1[6] is a typical PCN, which is coordinated by Cu2+ and trimesic acid and has two types of pore structures.

Since MOFs materials are synthesized from various organic ligands and metal ions, organic ligands can be combined with most transition metal elements including tetravalent metal ions to synthesize many new MOFs materials. According to incomplete statistical data, in the past 10 years, scientists have reported and studied more than 20,000 different MOFs. With the development of the MOFs family, the applications of MOFs materials are increasing year by year.

1.2 Overview of HOFs

HOFs are crystalline porous framework materials formed by connecting organic or metal-organic building units through hydrogen bonds[7-11]. In addition to hydrogen bonds, intermolecular forces such as π-π interactions, electrostatic interactions, and van der Waals forces also play a crucial role in the construction and stability of HOFs[12]. Research into HOFs has its origin in 1969. Marsh and Duchamp reported a crystalline compound with a hexagonal honeycomb-like hydrogen bond network structure using trimesic acid as the building unit[13]. However, in the following decades, the development of HOFs basically stagnated. It was not until the early 1990s that Wuest et al. reported a series of HOFs constructed by hydrogen bonds that HOFs materials began to develop slowly[14,15].

Since HOFs are constructed by hydrogen bonds, and the hydrogen bond force is generally weaker and more reversible than the coordination bond or covalent bond, HOFs materials have some unique advantages:

(1) The preparation conditions of HOFs are milder[16]. The preparation of HOFs usually only requires synthesis through recrystallization processes such as natural evaporation of the solvent, diffusion of the poor solvent into the good solvent, or precipitation of crystals by cooling the saturated solution.

(2) HOFs have better solution processing performance, so they are easier to be made into devices compared with COFs/MOFs. HOFs materials are constructed by intermolecular forces such as hydrogen bonds. Therefore, HOFs materials have good solubility in specific solvents, and when the solvent evaporates, HOFs may be recrystallized, endowing HOFs materials with solution processing performance. Sun Daofeng et al. reported the preparation of UPC-HOF-6 thin film using solution processing technology and applied the thin film to the pressure-responsive separation of H2/N2[17].

(3) HOFs materials have better self-healing and regeneration abilities. HOFs materials are constructed based on hydrogen bonds, and the flexibility and reversibility of hydrogen bonds endow HOFs with good self-healing and regeneration abilities. After multiple actual cycles of use, the frameworks of MOFs, COFs, and HOFs may be damaged to varying degrees, leading to a decrease in performance. The self-repair and regeneration of the structure are very important for the large-scale practical utilization of the materials. For example, Yuan Daqiang and Wu Mingyan et al. prepared a HOFs material (HOF-TCBP) with high stability and a large specific surface area. After gas adsorption, HOF-TCBP was dissolved in a small amount of DMF, and the regeneration of HOF-TCBP could be achieved by rotary evaporation. It is worth noting that the regenerated HOF-TCBP material has almost the same specific surface area as the original sample[18]. For another example, the UPC-HOF-6 thin film can even achieve self-repair of the structure under the treatment of a small amount of solvent[17].

(4) Since most HOFs materials do not contain metal ions, this metal-free property endows HOFs materials with better biocompatibility and lower cytotoxicity, making HOFs show great application potential in biological applications[19].

1.3 Applications of Organic Framework Materials

Since both MOFs/HOFs are crystalline porous materials containing organic components, they have some common characteristics. For example, theoretically, they both have large specific surface areas, diverse structures, adjustable pore shapes and sizes, and modifiable pore surfaces. Therefore, they are also widely used in various fields, such as gas storage, gas separation, catalysis, medicine, sensors, energy storage devices, etc.

In 2015, Eddaoudi and his colleagues reported a MOF named Alsoc-MOF-1 for methane storage[20].In 2016, Ghosh et al. first used porous HOFs materials as solid-state proton conduction materials. They self-assembled two porous HOFs materials (HOF-GS-10 and HOF-GS-11, Figure 1) by using 1,5-naphthalene disulfonic acid (S1) and 4,4'-biphenyl disulfonic acid (S2) with guanidine hydrochloride respectively[21].

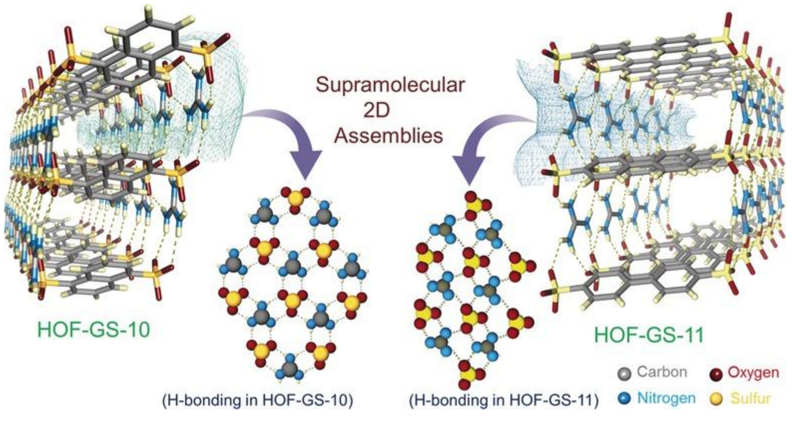

Figure 1 Two-dimensional Hydrogen Bond Framework of HOF-GS-10 and HOF-GS-11 Showing Hydrogen Bond Interactions Between Sulfonic Acid Groups and Guanidine Ions in the Two Compounds

In 2019, White, Falcaro, Doonan et al. reported a biocompatible HOF material (BioHOF-1) capable of encapsulating and protecting biomacromolecules. BioHOF-1 is self-assembled from polyamidine cations (M) and polycarboxylate anions (C6) in an aqueous solution. It has one - dimensional square open channels with a size of 0.64 nm×0.64 nm[22]. Xu's team integrated two lattice-mismatched MOF layers, Cu-HHTP (HHTP = 2,3,6,7,10,11-hexahydroxytriphenylene) and Cu-TCPP (TCPP = 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin), into a single system, Cu-HHTP@Cu-TCPP. This system is used for benzene sensing through van der Waals (vdW) interactions[23]. Chen et al. demonstrated the possibility of using zinc-imidazole ZIF-8 to control the delivery of the autophagy inhibitor 3-methyladenine. The loading amount of 3-methyladenine can be controlled by the amount of substances added during the synthesis process[24].

1.4 Limitations of Organic Framework Materials

Currently, the synthesis methods of MOFs are mainly limited to the molecular system. In fact, the synthesized MOFs are mainly polycrystalline solid powders, which cannot exhibit definite volume properties and anisotropy. People have been making efforts to cultivate large single crystals to fill this design gap.

N.Kim et al. achieved precise control of the local concentration gradient through a convection-free environment and a confined space, imitating the two main strategies of morphogenesis in biomineralization, namely spatial and morphological control (Figure 2). The growth kinetics and the evolution of crystal morphology were studied at the single crystal level, and the data were analyzed within the framework of the reaction-diffusion theory. This provides unique insights into revealing the development mechanism of complex morphologies, that is, local concentration gradients, physical constraints, and surface growth kinetics. In addition, continuous feeding of precursors under continuous flow can provide additional effective regulation of the size and shape of MOFs single crystals. This study shows that this bionic method can not only generate monolithic single crystals, but also effectively stack the soft porous network inside the microporous channels. Importantly, this result overcomes the problems related to the stacking and densification of materials, enabling their successful application in functional devices[25]. However, there are still significant challenges in the engineering of crystal growth and arrangement. Specifically, the growth of MOFs single crystals requires strict control of reaction conditions and the growth process, which is difficult; high-purity raw materials and precise experimental instruments are needed, resulting in high costs; due to the complexity and time-consuming nature of the engineering growth of MOFs single crystals, the yield is low; most importantly, the unfavorable mechanical properties of single crystals further limit their direct use. Therefore, tools or methods beyond crystal engineering are needed to promote the manufacturing of reticular MOFs materials towards higher complexity and functionality. The weak hydrogen bond force and poor directionality have significantly restricted the development of HOFs materials. Firstly, it is much more difficult to synthesize HOFs with the target structure than MOFs. Due to the weak hydrogen bond force and strong flexibility, the structure of HOFs is extremely vulnerable to external factors such as other intermolecular forces. Its final structure highly depends on the solvent used in the preparation and the synthesis conditions. For example, using TPE-4pn as the building unit, nine different structures of HOFs materials can be prepared in different solvents, and their porosities can range from 4% to 33.2%[26]. Using C3 as the building unit, complex structures with interlocking degrees of 18, 24, and 36 can be prepared under different conditions, and these structures cannot be accurately predicted before preparation[27]. Secondly, the stability of most HOFs materials is relatively poor. After removing the internal solvent in the pores, the framework is prone to collapse. Therefore, how to maintain the stability of the HOFs framework while removing the pore solvent remains a huge challenge.

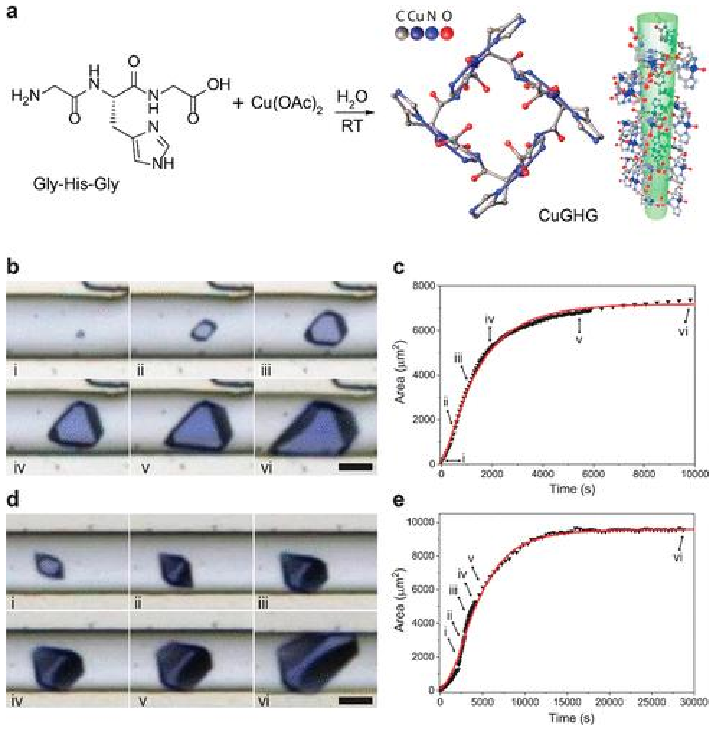

Figure 2 Growth of CuGH crystals in a closed microchamber (a) The chiral tripeptide GHG complex Cu2+ forms a three-dimensional frame CuGHG (b and d) are images taken at different times during the growth of two example CuGHG crystals 1 and 2, respectively. Roman numerals (i-vi) correspond to the selected time points in Figures c and e, respectively. The area-time plots corresponding to 50 μm (c and e) represent the growth dynamics of crystals 1 and 2, respectively, with symbols for experimental data and lines that best match the experimental data of the physical model based on reaction-diffusion theory

2 OVERVIEW OF METHODS FOR CHANGING THE PROPERTIES OF ORGANIC FRAMEWORK MATERIALS

Here, we mainly take the modification methods of MOFs as examples for illustration.

2.1 Post-Synthetic Modification (PSM)

MOFs are generally synthesized under solvothermal conditions at high temperatures (80-120°C) in low-vapor-pressure solvents such as DMF (DMF = N,N-dimethylformamide) or DEF (DEF = N,N-diethylformamide). Sometimes, modulators are added to control the specific size, morphology, or defect density of the resulting crystals[28-30]. Under these empirically derived reaction conditions, the diversity of functional groups that can be incorporated into MOFs is limited, and only includes those functional groups that can tolerate these relatively strict synthesis conditions. In order to expand the range of functional groups that can be introduced into MOFs and increase their versatility, post-synthetic modification (PSM) was developed and finally widely applied in this field. The key to successfully achieving PSM is that MOFs do not degrade during the reaction process and maintain their structure, crystallinity, and porosity. The key criteria for PSM on MOFs are similar to those of bioorthogonal chemistry, requiring a wise selection of reagents, reaction conditions, etc. for chemical transformation without harming or otherwise disrupting biomolecules or living cells[31,32]. PSM has many forms, but the main ones are covalent PSM and coordination PSM.

2.1.1 Covalent PSM

Covalent PSM refers to the modification of the organic linkers of MOF by reagents, generating new functional groups. This is equivalent to the functionalization of MOF, and this operation can change the properties of the material, including hydrophobicity, hydrophilicity, and catalytic behavior, etc.[33,34]. Generally, covalent PSM is achieved by using organic linkers derived from amines, aldehydes, or azides, because these moieties are highly reactive and can be rationally and selectively targeted by specific reagents[35-38].

For example, a professor in the United States pre-treated MOF with adipoyl chloride and successfully modified the active acyl chloride group onto the MOF to obtain an acyl-chlorinated MOF intermediate(Figure 3). Then, the ethyl acetate solution containing the MOF intermediate and caproyl chloride was added to the upper layer of the hexamethylenediamine aqueous solution, and post-synthetic polymerization was carried out at the interface between the two phases. The acyl-chlorinated MOF intermediate was connected to the formed polyamide fiber in the form of covalent bonds, and the obtained PA-66-UiO-66-NH2 composite material could be slowly pulled out from the interface to form continuous fibers. This material retained the flexibility of nylon-66 and exhibited excellent catalytic performance in the catalytic degradation of chemical warfare agents (CWA). Especially compared with the MOF connected by physical embedding rather than covalent bonds, its catalytic efficiency was almost an order of magnitude higher. This also shows that when preparing MOF-polymer composite materials, PSM that can achieve covalent bond connection has an absolute advantage over physical adsorption or embedding[39].

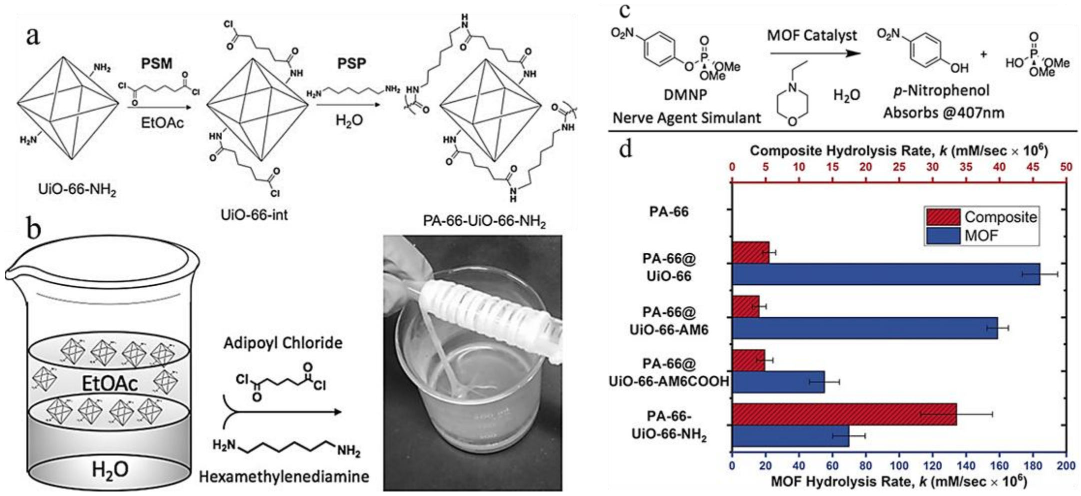

Figure 3 (a) Interface fabrication of PA-66-UiO-66-NH2 (b) PSP by PSM and PSP scheme (c) DMNP degradation reaction (d) Catalytic degradation rate of DMNP by MOFs powder and PA-66-MOF composite material, measured by UV/Vis absorption at 407 nm

2.1.2 Coordination PSM

Coordination PSM is to introduce organic molecules containing metal linkers onto the inorganic secondary building units (SBUs) of MOF. Starting from the observation of simple solvation and desolvation of the metal sites of SBUs, this PSM method has become the mainstream way to modify MO. During the revival of PSM in the late 2000s, typical coordination PSM strategies focused on using amines to coordinate the unsaturated sites in SBUs[40,41]. Recently, synergistic PSM with other linking molecules (such as carboxylates and phosphates) has been proven to effectively modify the surface of MOF crystals with polymers or biomacromolecules (such as nucleic acids or lipids)[42,43]. This surface coordination PSM method focuses on changing the macroscopic material properties of MOF while maintaining the unique framework properties of MOF, such as porosity, crystallinity, etc., thus producing unusual MOF-based materials, such as MOF-polymer hybrids and porous liquids.

Mirkin and his colleagues also used coordination PSM to connect phosphate-modified nucleic acids to the surface of MOFs. The results showed that oligonucleotides with terminal phosphate ligands were proven to coordinate with the SBUs of nine different MOFs containing multiple metals (Zr4+, Fe3+, Cr3+, and Al3+). All MOFs were characterized before and after PSM and showed a dense DNA surface coating. Importantly, the crystallinity and porosity of the particles were maintained after coordination PSM. In addition, the surface of gold nanoparticles (AuNPs) was covered with DNA sequences complementary to the surface of MOF, which enabled self-assembly as a function of the oligonucleotide sequence (**Figure 4**). This nucleic acid method was further used to demonstrate the applicability of MOFs as drug delivery carriers. MOFs usually cannot cross the cell membrane due to their inherent large size and charged surface. To overcome this limitation, a series of Zr4+-based nanoparticle MOFs were synthesized and incorporated with insulin, and then coordination PSM was carried out with phosphate-capped oligonucleotides to facilitate cell entry. Through the surface coating of oligonucleotides, insulin-loaded MOFs were proven to be able to transport across the cell membrane. This study shows that the synergistic PSM method provides ample opportunities for the development of highly functional MOF and cargo combinations for biomedical applications[44].

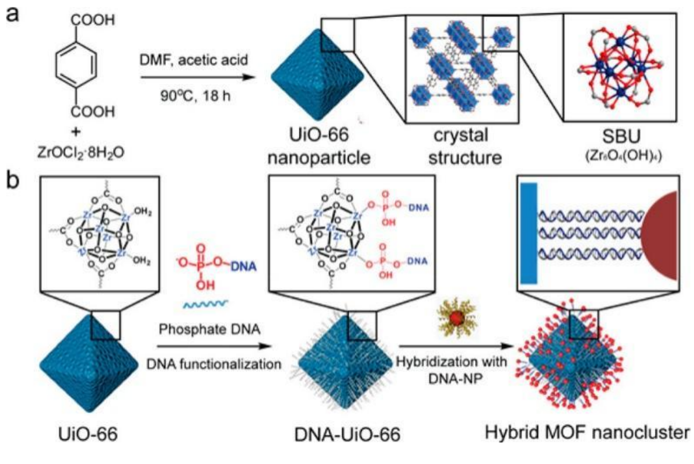

Figure 4 (a) Schematic diagram of the solvothermal synthesis of UiO-66 MOF nanoparticles (b) DNA modification of MOFs using terminal phosphoric acid modification of DNA and subsequent sequence-specific assembly of the MOF-NP core-satellite hybrid structure

2.2 Synthesis of Two-Dimensional Layered MOFs

Two-dimensional MOFs can combine the inherent advantages of MOFs with the excellent physical properties of ultrathin two-dimensional materials, improving and enhancing the performance of MOFs in numerous applications[45]. Therefore, exploring reliable methods for preparing ultrathin two-dimensional MOFs nanosheets is of great significance for in-depth research on their excellent properties and potential applications. Up to now, efforts have been made to develop effective synthesis methods for two-dimensional MOFs. Currently, there are mainly two types of preparation strategies: "top-down" and "bottom-up".

2.2.1 Preparation of two-dimensional nanomaterials by the top-down method

The top-down method is a representative strategy initially proposed, which is to exfoliate bulk MOFs into two-dimensional sheet structures through various physical and chemical means. This requires that the exfoliated bulk MOFs must have a layered structure[46]. Layered MOFs materials have relatively weak interlayer interactions, making it easy for the top-down method to overcome these interactions and prepare 2D MOFs nanosheets. According to different forces, the top-down method can be divided into physical exfoliation and chemical exfoliation.

(1) Physical Exfoliation Method

The physical exfoliation method uses various mechanical forces such as ultrasound and grinding to break down the weak interlayer interactions (van der Waals forces and hydrogen bonds) without breaking the covalent bonds in each layer, so as to maintain the structure of each layer. Therefore, it can also be called the mechanical exfoliation method.

Zamora and his colleagues reported the first example of the exfoliation of bulk MOFs. Using CuBr2, isonicotinic acid, KOH, and KBr as raw materials, a bulk black glossy crystal [Cu2Br(IN)2]n (IN = isonicotinic acid) was synthesized by the hydrothermal method, and the structure of [Cu2Br(IN)2]n was determined by single-crystal X-ray diffraction (XRD) technology[47]. As shown in Figure 5a, the 2D layered sheet is formed by the connection of a copper dimer with one bromine ligand and four isonicotinic acid ligands, that is, two ligands are coordinated through Cu-O bonds, and the other two ligands are coordinated through Cu–N bonds. Due to the π–π stacking between the aromatic rings of isonicotinamide groups, the stacking of these 2D layers along the a-axis leads to the final structure (Figure 5b). To prepare 2D [Cu2Br(In)2]n nanosheets, probe ultrasound was used as the mechanical force to overcome the interlayer π-π stacking. Atomic force microscopy (AFM) imaging showed that the obtained 2D nanosheets were very densely and uniformly distributed on highly oriented pyrolytic graphite[48]. The thickness of MOF-2 nanosheets is 1.5-6.0 nm, and the lateral size ranges from 100 nm to 1 µm. The exfoliation effect of different solvents on MOF-2 was studied, and acetone was found to be the solvent with the best exfoliation effect. Although the exact role of the solvent is still unclear, the surface energy of the solvent is considered to play a key role in the exfoliation of bulk MOFs, similar to the exfoliation of graphite[49]. Only a solvent with an appropriate surface energy can exfoliate graphite, resulting in a reasonable amount of graphene. Theoretical calculations have proven that if the surface energy of the solvent is close to that of graphene, the obtained graphene nanosheets can be effectively dispersed in this solvent due to the low driving force for reaggregation[49]. Other solvents, such as methanol[50], ethanol[51], isopropanol[52], and N,N-dimethylformamide (DMF)[53], have also been used for the exfoliation of 2D MOFs.

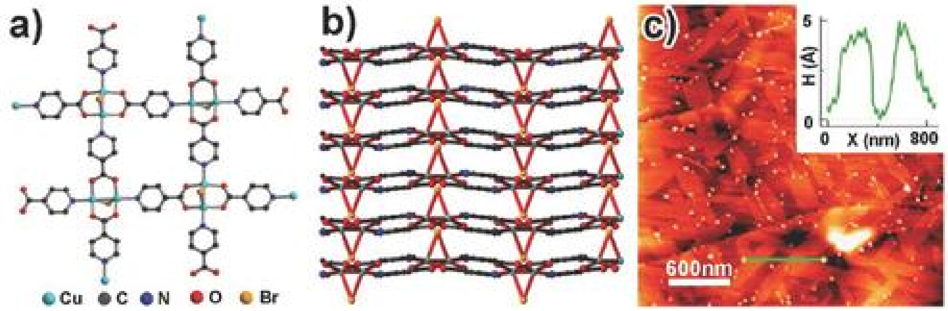

Figure 5 (a) Structure of single-layer [Cu2Br(IN)2]n nanosheets (b) and superposition of layers along axis a (c) AFM morphology of [Cu2Br(IN)2]n nanosheets deposited on HOPG

(2) Chemical Exfoliation Method

The chemical exfoliation method is a method that uses the in-situ chemical reaction of interlayer organic molecules in bulk layered MOFs to regulate the interlayer interaction, and obtain exfoliated ultrathin two-dimensional MOFs nanosheets with a high yield. Among them, the chemical intercalation exfoliation strategy is the most typical. The intercalation exfoliation technology is one of the most promising strategies for the large-scale production of atomic thin sheets, and it is favored because of its solution processability, scalability, and the products' large lateral dimensions and high single-layer yield[54,55]. Due to the structural characteristics of layered compounds, molecules or ions can be inserted between the layers of the bulk material to expand the interlayer spacing and weaken the interlayer interaction. According to the different intercalants, it can be divided into molecular intercalation and ionic intercalation.

When the molecular intercalation reaction is carried out in a solvent, small molecules can be inserted into the interlayer spacing of the layered compound to form a composite structure, and the expansion of the interlayer distance is conducive to further exfoliation[56]. In order to fabricate ordered two-dimensional metal-organic framework (MOF) nanosheets, Ding et al. proposed a method of embedding and chemical exfoliation through a reduction reaction. First, the ligand containing a disulfide bond was embedded into the layered MOFs by coordination insertion, and then the efficient exfoliation of the layered MOFs was achieved through the breaking of the disulfide bond, obtaining MOFs nanosheets with a thickness of about 1 nm and a yield of about 57%[57] (Figure 6).

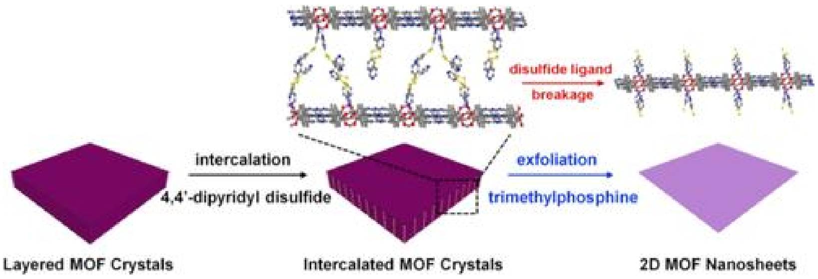

Figure 6 2D MOFs Nanosheets were Prepared by Sandwich Insertion and Chemical Stripping

The exfoliation process of MOF-Lns by Xia et al. is as follows: Suspend MOF-Lns in the n-hexane solution of n-butyllithium and stir it, and then centrifuge the MOF-Lns with inserted Li+ to finally prepare MOF-Lns nanosheets[58,59]. The intercalation and post-intercalation effects can overcome the interlayer adhesion of layered materials, thus facilitating subsequent exfoliation and delamination. This is the intrinsic mechanism of preparing atomic thin-layer materials by intercalation exfoliation. This post-intercalation effect may be manifested as an increase in the interlayer spacing[60], the release of bubbles, or an energetically favorable solvation process[61,62], which mainly depends on the types of intercalants and solvents used. The insertion of molecules (such as alkylamines[60]) is a charge -transfer-free process, which usually leads to a significant increase in the interlayer spacing. This post-intercalation effect weakens the van der Waals forces that cause interlayer adhesion, thereby promoting the exfoliation of atomic layers. The intercalation of ions is always accompanied by the charge transfer between the intercalated ions and the layered crystals, resulting in the formation of charged layers. This process reduces the interlayer van der Waals forces, but generates additional electrostatic attraction (stronger than the van der Waals forces[63]) between the ions with opposite charges and the layers. Therefore, the overall attraction between the layers increases, and the overcoming of these attractions is usually related to the solvent used in the exfoliation process. Protic solvents (such as water) usually lead to the release of gases (such as hydrogen[64,65], sulfur dioxide[66,67], and oxygen[68,69]), which will generate a large force to push the individual layers apart and play an important role in the exfoliation mechanism. Aprotic solvents can coordinate with the charged layers and ions, thus promoting the energetically favorable solvation process, which is also beneficial to the dispersion of atomic layers[61,62].

Compared with the physical exfoliation method, the yield of two-dimensional MOFs nanosheets prepared by the chemical exfoliation method has been increased, and the reproducibility has been improved to a certain extent. However, it is still difficult to precisely control the thickness and size of the materials. In summary, the top-down method is a simple and practical method for preparing two-dimensional MOFs nanosheets, but it has limitations. For example, the exfoliated crystals need to have a layered structure; the exfoliation process will damage the layered crystalline structure of the nanosheets; more importantly, the thickness distribution of the exfoliated products is uneven and the yield has always been low, making it difficult to achieve large-scale synthesis. Therefore, people have developed another bottom-up method as a supplement.

2.2.2 Preparation of two-dimensional nanomaterials by the bottom-up method

The bottom-up method is a method for gradually synthesizing ultrathin two-dimensional MOFs nanosheets through the coordination of metal cations and organic ligands, and its formation process mainly originates from the anisotropic growth of crystals. In this process, the growth rate of the high-energy surface in the lateral direction of the material is higher than that of the low-energy surface in the longitudinal direction, resulting in a preferential growth orientation of the two-dimensional material in the horizontal direction[70]. Therefore, the key to this method is to selectively limit the growth of MOFs in the vertical direction and only allow their lateral growth in the two-dimensional direction to adjust the growth rates of different crystal planes. The two-dimensional MOFs nanosheets prepared by this method have a uniform thickness and mild preparation conditions. Currently, several typical bottom-up methods include the solvothermal method[71], the interface synthesis method[72], the auxiliary synthesis method[73], and the two-dimensional oxide sacrificial method[74], etc.

(1) Solvothermal Method

The solvothermal method is one of the earliest and more classic methods for preparing MOFs materials. That is, mix metal salts, ligands, and other raw materials with water or other organic solvents, place them in a sealed container and heat them, and carry out the reaction under its own pressure to prepare two-dimensional MOFs nanosheets. Tian et al. successfully prepared MOFs nanosheets Cu2(CuTCPP) with a small molecular layer thickness [TCPP is 5,10,15,20-tetrakis(4-carboxyphenyl)porphyrin] with a high yield by a one-pot solvothermal method, in which Cu(NO3)2·3H2O and H2TCPP were reacted in N,N-dimethylformamide (DMF) at 85°C for 24 hours. The experiment found that high aspect ratio nanosheets with good dispersibility can be obtained at a lower concentration. When the ligand concentration and the metal salt concentration are lower than 6.0×10-4 mol/L and 2.0×10-3 mol/L respectively, the thickness of the obtained nanosheets is only 3.0 nm[75].

(2) Interface Synthesis Method

The interface synthesis method is to use the liquid/liquid or liquid/air interface to limit the growth of MOF nanosheets, that is, interface synthesis. In this method, the reaction occurs at the solvent interface, ensuring good control over the nucleation and growth of MOF, and using the well-dispersed monolayer of organic ligands on the liquid surface to control the thickness of MOF nanosheets. This method has been widely used to prepare MOF nanomaterials, such as NAFS-1 and NAFS-2 nanofilms[76,77] and nickel bis(dithiolene) and cobalt bis(dithiolene) nanosheets[78,79].

Generally, Nishihara and his colleagues have reported the synthesis of single-layer and few-layer nickel bis(dithiolene) nanosheets (denoted as Nano 1) through the coordination reaction of nickel(II) acetate and benzenehexathiol (BHT) at the liquid-gas interface[78]. As shown in Figure 7a, a thin layer of ethyl acetate solution containing BHT was gently spread on the surface of an aqueous solution containing Ni(OAc)2 and NaBr. After the evaporation of ethyl acetate, Nano 1 nanosheets were obtained at the liquid-gas interface and then transferred to HOPG. Scanning tunneling microscopy (STM) imaging clearly showed the hexagonal pattern of single-layer Nano 1 nanosheets with a height of 0.6 nm (Figure 7 b,c), which was also confirmed by atomic force microscopy (AFM) (Figure 7 d,e). Recently, the same research group found that by changing the concentration of the ligand, the thickness of the nanosheets can be adjusted in the range of 6-800 nm, demonstrating the feasibility of this method[80].

The conditions of interface synthesis are relatively mild and can be carried out at room temperature and normal pressure. However, due to the limited area of the interface region, the yield of the obtained two-dimensional MOFs nanosheets is often low.

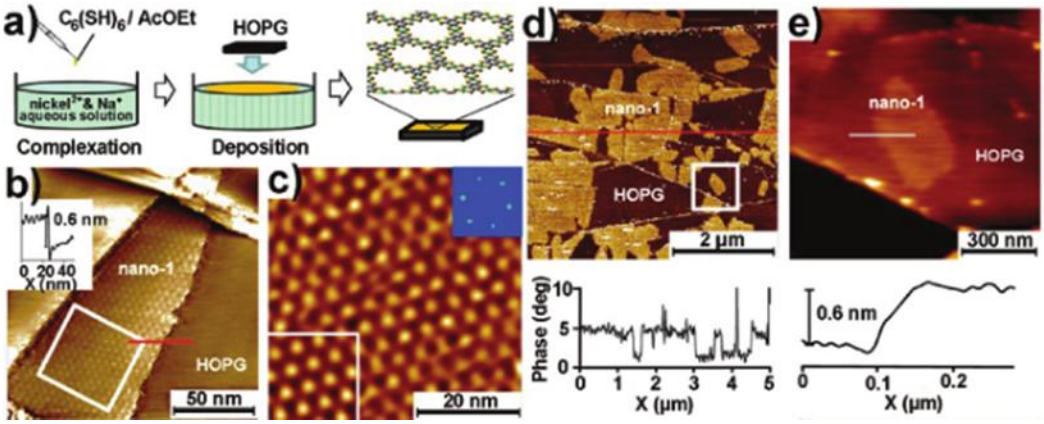

Figure 7 (a) Schematic diagram of the synthetic route of the nanometer-1 nanosheet (b) STM topological image of the single-layer nanometer-1 nanosheet on the HOPG (illustration: Height outline along the red line) (c) (b) Enlarged image of the white square (illustration: Speed Fourier Transform (FFT) of STM images (d) AFM phase image and its cross section analysis on HOPG (e) AFM topological image and height distribution of single-layer nanosheets along white lines

(3) Auxiliary Synthesis Method

The auxiliary synthesis method is to limit the growth direction of crystals by adding various auxiliary agents as capping agents, promoting the anisotropic growth of crystals, and thus facilitating the synthesis of two-dimensional MOFs nanosheets[81,82].

As is well known, Zn-TCPP (TCPP = tetrakis(4-carboxyphenyl)porphyrin) MOFs are constructed by stacking two-dimensional lamellae, which are formed by connecting a Zn2(COO)4 paddlewheel metal node with four TCPP ligands (Figure 8a)[83]. In the traditional synthesis method, without adding surfactants, only bulk Zn-TCPP crystals can be synthesized. However, in the presence of the surfactant, polyvinylpyrrolidone (PVP), ultrathin Zn-TCPP nanosheets have been obtained. PVP can selectively attach to the surface of MOFs, which stabilizes the Zn-TCPP nanosheets and restricts their growth in the vertical direction, resulting in the formation of ultrathin Zn-TCPP nanosheets (Figure 9a). Fourier transform infrared spectroscopy (FTIR) confirmed the role of PVP. The results showed that after PVP was mixed with Zn(NO3)2, the stretching vibration at vC=O = 1662 cm-1 shifted to 1619 cm-1, indicating a strong interaction between the C=O group in PVP and Zn2+. Based on atomic force microscopy (AFM) measurements, the thickness of the Zn-TCPP nanosheets is 7.6±2.6 nm. The low contrast of the Zn-TCPP nanosheets shown in the transmission electron microscopy (TEM) images also confirms their ultrathin nature (Figure 8b). The crystal structure of the Zn-TCPP nanosheets was confirmed by selected area electron diffraction (SAED) (the inset in Figure 8b), which is in good agreement with the X-ray diffraction (XRD) and theoretical results. The surfactant-assisted synthesis method can be used to prepare various two-dimensional MOFs nanosheets, such as Cu-TCPP nanosheets, Cd-TCPP nanosheets, and Co-TCPP nanosheets (Figure 8c-e).

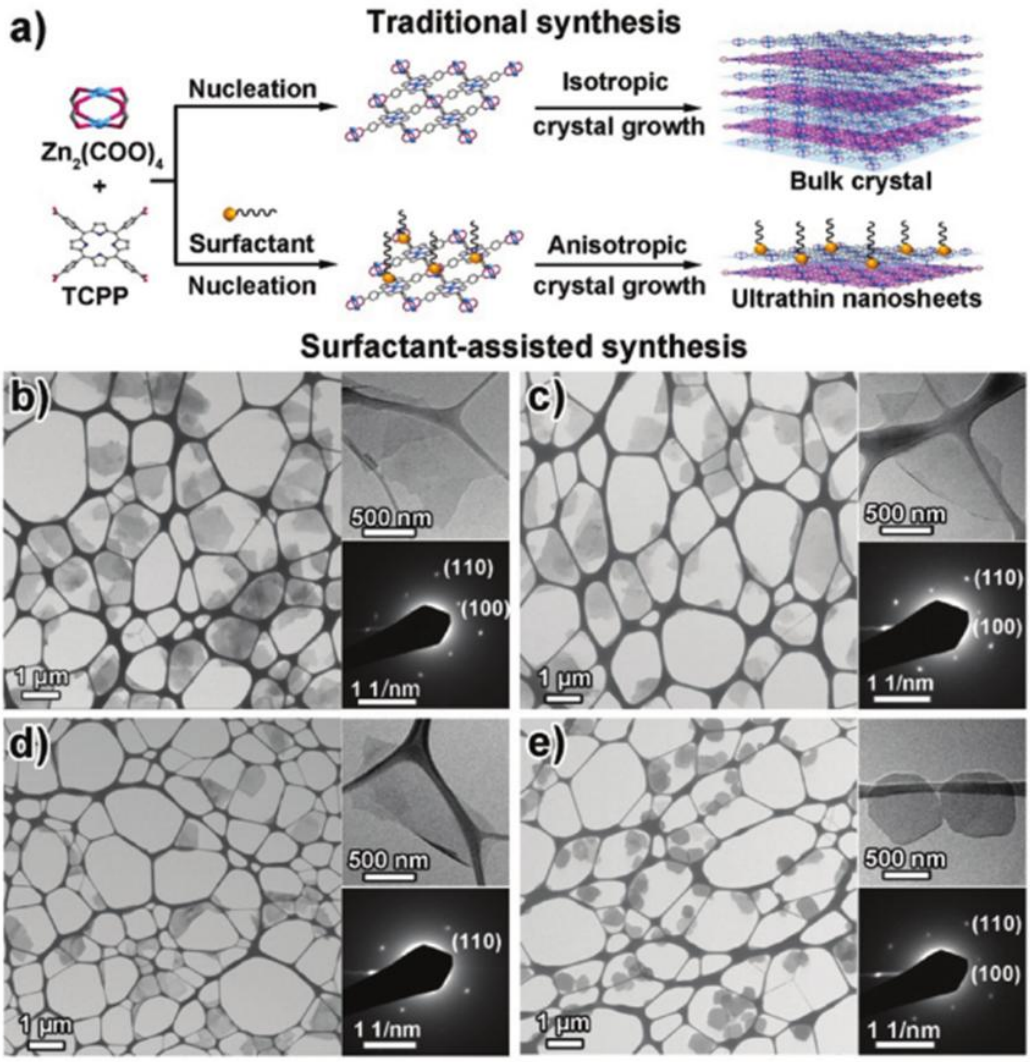

Figure 8 (a) Traditional synthesis of Zn-TCPP-MOF and surfactant-assisted synthesis with MOF layers drawn in blue and purple, respectively, to make the layered structure clearly visible (b) Zn-TCPP nanosheets (c) Cu-TCPP nanosheets (d) Cd-TCPP nanosheets (e) STEM images of Co-TCPP nanosheets

3 CONCLUSION

MOFs and HOFs in organic framework materials exhibit unique properties and application potential. In terms of synthesis, the synthesis methods of MOFs are constantly evolving, and the PSM technique expands their functionalization possibilities. However, currently synthesized MOFs are mostly polycrystalline powders, and it is extremely difficult to prepare large single crystals, facing issues such as stringent reaction conditions, high costs, low yields, and poor mechanical properties. Although HOFs have advantages like mild preparation conditions and solution processability, the weaknesses of hydrogen bonds make it difficult to synthesize target structures and result in poor stability.

Among the preparation strategies for two - dimensional MOFs, the "top-down" method is easy to operate, but the quality and yield of products are limited. The "bottom - up" method can precisely control the thickness of nanosheets. Nevertheless, methods like the solvothermal method, interface synthesis method, and auxiliary synthesis method have drawbacks such as high - requirement reaction conditions and low yields respectively. Future research should focus on developing more efficient synthesis techniques to overcome the limitations of existing methods and optimize material properties. This will not only contribute to a deeper exploration of the characteristics of organic framework materials but also promote their wide application in fields such as gas storage, catalysis, and biomedicine, enabling them to better meet practical needs and achieve large-scale industrial production.

COMPETING INTERESTS

The authors have no relevant financial or non-financial interests to disclose.

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