

# Synthesis and application of metal-organic frameworks

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**Abstract.** Metal-organic frameworks (MOFs) are an intriguing class of materials that undergoes self-assembly, originating from polydentate organic ligands. These ligands are primarily composed of aromatic polynucleic acids and polybases, along with transition metal ions. The advancements in MOFs have diversified, employing ligands based on carboxylates or nitrogen-containing heterocyclic organic neutral ligands, resulting in materials characterized by their increased porosity and remarkable chemical stability. The research provides a comprehensive review of conventional and alternative synthesis methods, highlighting recent techniques such as microwave-assisted, electrochemical, mechanochemical, and sonochemical synthesis. The synthesis methods are discussed in detail, to provide a comprehensive understanding of the various techniques available. The versatile properties of MOFs find applications in various fields such as gas adsorption, chemical sensing, catalysis, and drug delivery. The analysis not only deepens the understanding of MOFs' present state but also inspires future innovations in their synthesis and applications. The research also highlights the potential of MOFs in drug delivery, where they can be used as carriers for the delivery of drugs or other therapeutic agents. The comprehensiveness of this research provides a valuable resource for understanding the current state of MOFs research and identifies future directions for innovation in their synthesis and applications.

**Keywords:** metal-organic frameworks, synthesis, application.

## 1. Introduction

Metal-organic frameworks (MOFs) represent coordination polymers that undergo self-assembly, originating from polydentate organic ligands, mainly comprising aromatic polynucleic acids and polybases, in conjunction with transition metal ions. Despite the initial synthesis of the first MOFs dating back to the mid-1990s, their porosity and chemical stability were found to be suboptimal. Consequently, researchers delved into the exploration of coordination polymers formed by innovative cationic, anionic, and neutral ligands. In the present context, a variety of MOFs materials has been successfully synthesized, primarily employing carboxylate-based organic anionic ligands or in tandem with nitrogen-containing heterocyclic organic neutral ligands [1-3]. Notably, the majority of these MOFs exhibit remarkable attributes, characterized by elevated porosity and commendable chemical stability. This evolution underscores the ongoing refinement and diversification of MOFs, positioning them as promising candidates for different applications within the field of materials science.

Diverse methods exist for the synthesis of MOFs, with recent years witnessing the emergence of several novel techniques. Among the prominent approaches, the solvent method and liquid-phase diffusion method stand out as primary contenders. Additionally, recent advancements have introduced innovative preparation methods such as the sol-gel method, stirring synthesis method, solid-phase synthesis method, as well as techniques involving microwave, ultrasonic, and ionic heat.

MOFs possess a range of outstanding properties, including porosity, a substantial specific surface area, and abundant metal sites. Consequently, their widespread adoption in chemistry and chemical engineering has become evident. Notably, MOFs find utility in areas such as gas storage, molecular separation, catalysis, and the controlled release of drugs. These remarkable attributes position MOFs as a formidable resource in addressing challenging issues within the fields of chemistry and chemical engineering. Their versatility and unique characteristics make them a potent tool for tackling a myriad of complex problems in these fields.

This research will mainly focus on reviewing the methods of synthesis and potential application of MOFs. This comprehensive analysis not only facilitates a deeper understanding of the present state of MOFs in synthesis methods and applications but also serves as a source of inspiration for future innovations. By delving into the intricacies of synthesis techniques and the diverse array of applications, researchers gain valuable insights that can catalyze innovative strides in the development of next-generation MOFs.

## 2. Conventional synthesis

Conventional methods for synthesizing MOFs are usually solution-based or hydrothermal. These methods operate at room temperature, are relatively simple, and are suitable for large-scale preparation. Hydrothermal methods require high temperatures and pressures, usually in the presence of water. In contrast, the reaction conditions are more severe, requiring high temperatures and pressures, but this facilitates the formation of MOFs with more complex pore structures. The reaction is performed in a high-pressure vessel, and the hydrothermal conditions induce the rapid reaction of metal ions and organic ligands in aqueous phase to form the MOFs. The hydrothermal method reacts at a relatively fast rate, which facilitates the rapid formation of crystals. Due to the high temperature and high-pressure conditions, hydrothermal methods are often used to prepare MOFs with special structures and properties, such as those with small pore sizes. The use of water as the reaction medium in this method is relatively environmentally friendly, as water is a green solvent.

The solution method can be carried out at room temperature or relatively low temperatures, and generally does not require high temperature and pressure conditions. The reaction conditions are relatively mild and are suitable for various combinations of metals and organic ligands. The reaction is usually performed in solution, where the metal salt and organic ligand are mixed in a solvent and made to mix well by means of stirring. The formation of MOFs is more gradual, and the structure of the product can be controlled by modulating the reaction conditions. It is suitable for a wide range of metal and organic ligand combinations, and can be used to synthesize MOFs under relatively simple conditions. It is suitable for some organic ligands that are more sensitive to the reaction conditions. Some common organic solvents are usually used in this method, so it may be better for environmental friendliness.

Outstanding MOFs, including MOF-5, MOF-74, MOF-177, HKUST-1, or ZIF-8, can be obtained at room temperature by simply mixing starting materials [1-3]. This technique is occasionally termed a direct precipitation reaction, signifying that the crystallization of specific MOFs must occur within a short time frame. Notably, certain MOFs, such as ZIF-8, manifest commendable thermal stability and chemical stability. Alterations in reaction temperature significantly influence product formation, typically resulting in more compact structures at elevated temperatures. In specific systems, elevating the reaction temperature is imperative to attain the desired crystallinity and reaction rate, especially when employing more inert ions from a kinetic perspective. Nonetheless, temperature exerts a profound influence on crystal morphology, and extended reaction durations may potentially induce the degradation of MOFs.

## 3. Alternative synthesis

Chemical reactions require specific energy input. This energy is frequently supplied through conventional electrical heating, involving heat transfer through convection from an oven. Alternatively, energy can be introduced through various methods like electromotive force, electromagnetic radiation, or mechanical waves (ultrasound). Various approaches may lead to unique compounds unattainable by other means. Alternative routes can produce compounds with diverse size and morphologies, impacting the material's properties.

### 3.1. Microwave-assisted synthesis

Microwave-assisted method for the synthesis of MOFs is an efficient and rapid synthesis method. In conventional synthesis methods, temperature and reaction time may be the limiting factors for the synthesis efficiency. In contrast, the microwave-assisted method can significantly shorten the synthesis cycle by increasing the temperature of the reaction system in a short period of time. Microwave radiation can act directly on the reacting substances to absorb energy more uniformly, thus accelerating the reaction rate. In addition, the microwave-assisted method has the advantage of mild reaction conditions, which helps to maintain the structure and properties of MOFs. This is because microwaves are able to initiate and accelerate the reaction at lower temperatures, reducing unwanted side reactions or pyrolysis and contributing to the formation of high-quality MOFs.

### 3.2. Electrochemical synthesis

For the electrochemical synthesis of MOFs, the primary goal was to eliminate negative ions like nitrates, perchlorates, or chlorides during the synthesis process, concerning in mass manufacture processes. Instead of using metal salts, metal ions can be introduced into the reaction medium through anodic dissolution, which contained dissolved linker molecules and conductive salts. Using native solvents avoided the sedimentation of metal on the positive pole but resulted in the generation of H<sub>2</sub> in this process. Another approach involves the use of compounds that are preferentially reduced, such as acrylonitrile, acrylates, or maleic esters. Other advantages of this electrochemical process include the ability to carry out consecutive processing and achieve larger solid concentration in comparison to conventional intermittent reactions.

### 3.3. Mechanochemical synthesis

Mechanical force possesses the capability to incite diverse physical phenomena (pertaining to mechanical physics) and instigate chemical reactions. Within the realm of mechanochemical synthesis, the mechanical disruption of intra-molecular bonds gives rise to consequential chemical alterations. This groundbreaking approach was initially documented in 2006 for porous MOFs preparation. In the process of mechanochemical synthesis, methodologies such as ball milling or shaking are conventionally utilized to introduce mechanical energy. The infusion of this mechanical energy not only furnishes the essential activation energy for the reaction but also facilitates adjustments to the temperature and pressure conditions inherent in the reaction system. Ball milling, a prevalent technique in mechanochemical synthesis, entails the mechanical treatment of reaction materials using balls within a milling jar. This treatment serves the dual purpose of homogenizing the reaction materials and supplying ample mechanical energy to catalyze the reaction. Conversely, shaking involves the transmission of mechanical vibrations through a shaking device, culminating in the synthesis of MOFs. The appeal of mechanoactivated MOFs synthesis is multifaceted. Environmental considerations play a pivotal role, with reactions transpiring at ambient temperature under solvent-free conditions, presenting a notably sustainable advantage. This methodology obviates the need for solvents, resulting in concise reaction times typically ranging between 10-60 minutes, yielding quantitatively and typically furnishing products with minute particles. Moreover, in select instances, metal oxides may supplant metal salts as starting materials, engendering water formation as a concomitant outcome. In contrast, the utilization of metal oxides in solvent-based reactions is infrequent because of their limited solubility. In addition, mechanochemical synthesis also holds environmental advantages, as the reactions can take place at room temperature without the need for solvents. This contributes to a reduction in adverse environmental impacts, making this method highly regarded in the field of green synthesis.

### 3.4. Sonochemical synthesis

Sonochemical synthesis in MOFs involves a method utilizing ultrasound as an excitation source during the fabrication process. This approach utilizes the mechanical vibrational energy of ultrasound to enhance reaction rates, improve product purity, and partially influence the crystalline structure of

the synthesized materials. Sonochemical synthesis has been widely applied in the preparation of MOFs, providing an innovative approach for their rapid and efficient synthesis. In sonochemical synthesis, ultrasound is propagated through a liquid medium into the reaction system, inducing vibrational and collisional effects among molecules. This mechanical action can overcome various limitations in the reaction, such as diffusion restrictions between solid particles, thereby promoting the mixing and reactions between reactants. Moreover, ultrasound's action can induce localized changes in temperature and pressure, further facilitating the formation of MOFs. The benefits of sonochemical synthesis for MOFs encompass reduced reaction times, elevated yields, enhanced crystallinity of the products, and regulated control over crystal size distribution. This method exhibits substantial potential, particularly for MOFs presenting challenges in conventional synthesis methods, notably in forming large crystals or synthesizing under restrictive conditions.

## 4. Applications

Their chemical tunability, extremely high specific surface area and porosity, unlimited number of metal-ligand combinations, ease of synthesis and characterization, and low cost have led to a diverse of various applications of MOFs in the fields of adsorption, chemical sensing, catalysis and drug delivery. This research will discuss these applications in detail.

### 4.1. Gas adsorption and separation

MOFs possess distinctive properties that render them well-suited for gas adsorption and separation applications. These materials exhibit numerous pores and channels, providing an expansive surface area for efficient gas adsorption and storage. The size of the pores in MOFs can be intentionally adjusted by selecting different metal ions and organic linkers, enabling the selective adsorption of specific gas molecules based on their size and shape. MOFs demonstrate a high adsorption capacity for gas molecules due to their extensive surface area and the presence of open metal sites within the framework. Furthermore, their tunability and selectivity result from interactions between target gas and the MOFs materials. MOFs can be easily regenerated by desorbing adsorbed gas molecules under mild conditions, such as heating or reducing the pressure, making them suitable for repeated use in gas separation processes.

In summary, the unique properties of MOFs position them as promising materials for diverse gas adsorption and separation applications. These applications encompass the separation of CO<sub>2</sub>/CH<sub>4</sub> mixtures to capture CO<sub>2</sub> from industrial emissions. This selective adsorption for the prepared MOFs-based materials has also been observed in other functional materials such as Cu(hfipbb)(H<sub>2</sub>hfipbb)<sub>0.5</sub> [4], Zn(tbip) [5], and Zn(bdc)(ted)<sub>0.5</sub> [6].

### 4.2. Chemical sensing

MOFs find extensive applications in chemical sensing, and their distinctive structure and properties render them excellent materials for chemical sensors. They can be employed to detect metal ions by forming stable complexes with them through coordination. The intentional design of MOFs structures allows for highly selective detection of specific metal ions, including copper ions and iron ions. Serving as ion-selective sensors, MOFs achieve selective recognition of specific ions through functionalized groups on their surfaces. This selectivity contributes to the development of sensors enabling highly sensitive detection of specific ions in environmental or biological systems.

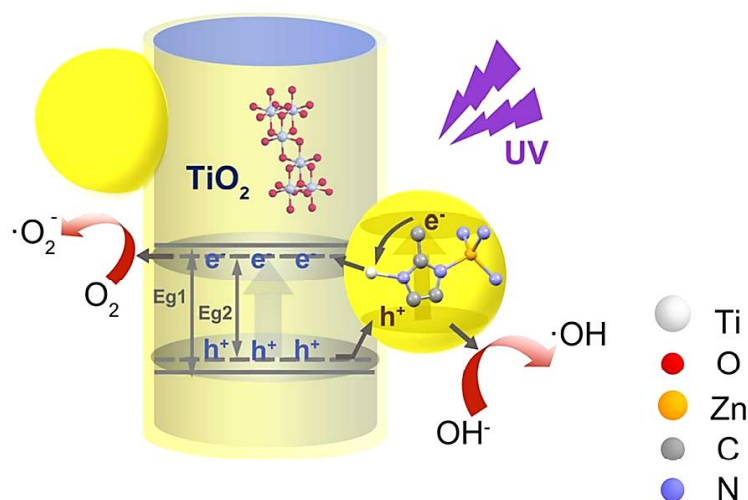
Certain ligands in MOFs possess fluorescent properties, enabling the design of fluorescent sensors for highly sensitive detection of specific molecules. The fluorescence intensity or wavelength of fluorescent MOFs can be altered by the presence or absence of receptor molecules to facilitate the detection of target molecules. Additionally, the structure and surface functionalization of MOFs respond to pH changes, making them ideal for pH-sensitive sensors. MOFs can indicate pH through pH-induced structural changes or fluorescence changes of specific luminescent ligands. Moreover, MOFs hold potential applications in photoelectrochemical sensing for the detection of specific

molecules or catalytic reactions. Their conductivity and optical properties can be intentionally modified to meet the requirements of various sensors.

### 4.3. Catalysis

Due to their unique properties, MOFs find widespread application in catalysis, serving as primary catalysts or co-catalysts in diverse reactions. MOFs function as enzyme mimics, encapsulating enzymes in their porous structures to provide a stable and controlled environment for enzymatic reactions. For instance, reactors like enzyme@ZIF-8 have been developed by embedding enzymes in ZIF-8 and have proven successful in catalytic reactions, including the reduction of pyruvic acid to lactic acid. In addition, MOFs can function as co-catalysts in photocatalysis, exhibiting semiconductor-like properties as photosensitizers that absorb light to generate charge carriers. Subsequently, these charge carriers transfer to active sites for additional reactions, such as hydrogen production, organic transformation, and water splitting. MOFs can establish heterojunctions with semiconductors, improving charge transfer and catalytic performance. MOFs offer additional functionalities in photocatalytic systems, extending light absorption and expediting charge transfer in composites containing noble metal nanoparticles. They also enhance the photothermal effect and facilitate the generation of reactive species, such as singlet oxygen, in collaboration with other catalytic materials.

Luo et al. utilized electrostatic spinning to decorate ZIF-8 onto TiO<sub>2</sub> nanofibers, creating a TiO<sub>2</sub>/ZIF-8 hybrid photocatalyst. This hybrid photocatalyst exhibits significant photocatalytic ability for the photodegradation of Rhodamine B (RhB), which is attributed to the N–Ti–O bond, which reduces the recombination of electron–hole pairs [7, 8]. As shown in Fig. 1, photocatalytic mechanism of the prepared TiO<sub>2</sub>/ZIF-8 nanomaterials was further analyzed.



**Fig. 1** Photocatalytic mechanism for the prepared TiO<sub>2</sub>/ZIF-8 nanomaterials [8].

### 4.4. Drug delivery

MOFs find application in drug delivery owing to their unique properties. First, MOFs possess substantial surface area and specific pore sizes, facilitating a high drug loading capacity. This allows for the encapsulation of a considerable amount of drug within the MOFs structure. Second, MOFs can be tailored to exhibit controlled drug release properties. The drug release can be triggered by external stimuli such as pH, temperature, or the presence of specific ions. This permits precise control over drug release, ensuring optimal therapeutic effects. Third, MOFs can safeguard the encapsulated drug from degradation or premature release. The porous structure of MOFs acts as a shield, protecting the drug from external factors like enzymes or pH changes that could lead to degradation or inactivation. Fourth, for targeted drug delivery, MOFs can be functionalized with targeting ligands or antibodies for the precise delivery of the drug to the desired site in the body. This enhances the efficacy of the drug and mitigates side effects by minimizing exposure to healthy tissues. Fifth, for

biocompatibility, MOFs can be intentionally designed to be biocompatible, signifying their non-toxic nature and absence of adverse effects in the body. This is a crucial attribute for any material employed in drug delivery applications.

MIL-53 (Fe) MOFs constructed using  $\text{Fe}^{3+}$  and 1,4-benzenedicarboxylic acid for delivery of pibucaine with a drug loading of 20 wt% [9]. Zn-CDDB (Zinc-CDDB) exhibits promise as a drug delivery system, demonstrated in a study using it as a nanocarrier for 5-fluorouracil (5-Fu) delivery to HepG2 and MDA-MB-435s cell lines, achieving a loading percentage of 53.3 wt% and controlled release over 3 days [10].

## 5. Conclusion

This research comprehensively explores conventional and alternative synthesis methods for MOFs, spotlighting contemporary approaches like microwave-assisted, electrochemical, mechanochemical, and sonochemical approaches. Combined with their versatile properties, MOFs find applications in gas adsorption, chemical sensing, catalysis, and drug delivery. The analysis not only enhances understanding of MOFs' current state but also ignites inspiration for future innovations in synthesis and applications. MOFs, with their intrinsic flexibility, emerge not only as materials of academic interest but also as catalysts for transformative solutions across scientific domains. However, it is imperative to acknowledge potential challenges, such as limitations in stability, high preparation costs, and scalability issues, which must be overcome for MOFs to fulfill their promising role in practical applications. The unfolding journey of MOFs promises an exciting trajectory in advanced materials and their multifaceted applications.

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