

Review

Recent progress in the syntheses of mesoporous metal–organic framework materials

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ABSTRACT

Metal–organic frameworks (MOFs), which are constructed from the assembly of metal ions or metal clusters with organic linkers, represent a new class of crystalline porous materials with potential applications in the fields of gas storage and separation, heterogeneous catalysis and chemical sensing. The development of reliable and reproducible methods to fabricate MOFs with high stability and mesopore characters remains a great challenge to meet many future applications for separation, large molecules adsorption, drug delivery and size-selective catalysis and so on. In this tutorial review, we are mainly focusing on the recent developments in the fabrication of hierarchically structured MOFs based on nanoscience techniques.

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1. Introduction

Metal–organic frameworks (MOFs), also known as crystalline porous coordination polymers, are a new development on the interface between coordination chemistry and materials science [1–4]. They are inorganic–organic hybrid solids where metal nodes or polynuclear secondary building units (SBUs) are self-assembled to form a periodic and porous framework. This depends strongly on the coordination preference of the metal ions and the length and rigidity of the organic ligands [5–10]. Their diverse fascinating structural topologies, permanent porosity, and wide range of potential applications for gas storage [11–13], photochemistry [14–16], catalysis [17–21], and sensing [22,23] recently compelled a tremendous interest for this new class of porous material.

Like zeolites, MOFs are crystalline inorganic–organic hybrid materials with the atomic periodicity extending to the pores and channels. In zeolites, however, the periodic walls form from the condensation of silicate precursors with templating agent [24,25]. MOFs form via the self-assembly of SBUs and organic ligands. The self-assembly is strongly dependent on the coordination preference of the SBUs and the length and rigidity of the linkers under different reaction conditions including solvent types, reaction temperatures and times, and metal ion-to-organic ligand ratios. Various metals and ligands with different synthetic methods have already produced numerous possibilities of MOF materials [26–29]. Currently there are more than 15,000 MOFs on record at the Cambridge Crystallographic Data Centre with more than five MOF papers published per day within the past few years [30]. However, despite their versatility and rich chemistry, most MOF materials reported to date are microporous (pore sizes <2 nm) [31–33]. The small pore aperture inherently hinders the diffusion of bulky molecules and limits their interactions with the active sites within MOF structures. A significant number of research studies have been devoted to the preparation of hierarchically structured MOFs. These studies have been in line with tailoring MOF materials for new applications by hosting large objects and anchoring molecular functions.

Hierarchically structured MOF materials have attracted considerable interest because of their potential applications in large molecule adsorption and separation, bulky drug delivery, and heterogeneous catalysis [34–36]. The shape, size, and chemical environment of the mesopores within MOF framework matrix are of paramount importance for the aforementioned applications. In these applications, mesopores or macropores have specific performance in fast molecular diffusion and mass transfer [37–39]. In addition, microporous MOFs would also benefit from having additional mesopores to increase the accessibility to the microporous cavities containing the metal centers. Therefore, the presence of mesopore engineering in the microporous MOF networks markedly expands their use as a host to accommodate bulky molecules for anchoring molecular catalysts or for impregnation of active precursors or large drug molecules. This allows for their free reaction or transformation without diffusion limitations in a confined space. Most notably, the fabrication of mesopores in microporous MOFs combines the benefits of nanoporous materials with the advantageous properties of the parent microporous MOF materials. This may not only combine the respective valuable characters of micropores and mesopores or even the macropores components but will also often exhibit exceptional properties that exceed what would be expected from a simple mixture of the components [40–43].

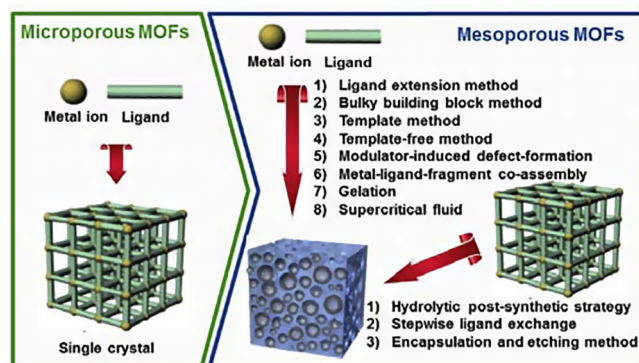
Although reviews about mesoporous MOF fabrications by using elongated organic ligands or based on supramolecular templating were reported [44,45], recently a few promising synthetic strategies have been developed. This tutorial review focuses on recent advances in the synthesis and fabrication of mesoporous metal–or-

ganic frameworks using nanoscience techniques. This review also discusses the future outlook for this field in the context of current challenges in the synthesis of hierarchically structured porous MOF materials.

2. Mesoporous MOF construction concept

In order to expand the pore widths of MOFs, a ligand extension method involving the use of longer organic ligands has been demonstrated. The final cavities of some specific MOFs could reach widths of 9.8 nm by increasing the length of organic linker to 5 nm [46]. Indeed, the elongated ligands need multiple-step synthesis and unfortunately pores of open MOFs built from this method are usually occupied by guest molecules that must be removed to induce a permanent porosity and possibly causing the structural collapses. Another difficulty in the fabrication of high porous MOF materials by ligand extension method is that the final MOFs are often accompanied by structural interpenetration that drastically reduces the size of the pores. An alternative way to fabricate mesoporous MOFs involves building block enlargement such as a bulky supramolecular building block (SBB), which has more complexity and higher connectivity in larger length scales resulting in a larger pore size in the MOF structures [15,47]. For example, in building MIL-100(Cr), μ 3-oxo bridged trimeric chromium (III) octahedral building units serve as SBUs and are connected by terephthalate ligands to afford a super tetrahedron in which the trimers occupy the four vertices. The connection between the microporous super tetrahedrons through vertices produces a highly porous network with two kinds of nanosized cages. The two nanosized cages has a 2:1 ratio and the smaller cage composed of 20 super tetrahedrons has an internal diameter of 2.9 nm while the larger cage containing 28 super tetrahedrons consists of an internal diameter of 3.4 nm [48]. Moreover, the combination of mixed ligands also proved to be a useful method to create mesoporous MOF materials with tuneable porosity [43,49]. However, the latter two methods strongly depend on the spontaneous association of metals and organic linkers and this self-assembly process is too elusive to control with the construction of mesoporous MOFs only sporadically happening.

Recently, novel approaches were explored to generate defects in the long-order structure of MOF single crystals, resulting in hierarchically structured MOF materials. These include ligand extension method [50–56], template method [57–61], template-free method [62–65], supercritical fluid synthesis [66–68], post synthetic strategy [69–71], metal-ligand-fragment co-assembly [72,73], modulator-induced defect formation strategy [74], and encapsulation and etching method [75,76]. These novel methods for mesopore



Scheme 1. Conceptual illustrations for mesopore fabrication in MOF.

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