

Metal organic frameworks for energy storage and conversion



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ABSTRACT

Metal–organic frameworks (MOFs), a novel type of porous crystalline materials, have attracted increasing attention in clean energy applications due to their high surface area, permanent porosity, and controllable structures. MOFs are excellent precursors for the design and fabrication of nanostructured porous carbons and metal oxides, especially for hierarchical nanostructures. In this review, the recent development and understanding of MOFs and MOF-derived nanomaterials in the applications of fuel cells, batteries (e.g. lithium-ion, lithium–sulfur, and lithium–air batteries), and supercapacitors are summarized in detail. In particular, we focus on the design and fabrication of the morphology of nanomaterials derived from MOFs and the significant impact of structure on the electrochemical performance in clean energy applications. Finally, we also present the future trends, prospects, and possible obstacles of the development of advanced MOFs and MOF-derived nanomaterials for more promising and large-scale commercial applications of clean energy.

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1. Introduction

1.1. Metal organic frameworks

Metal–organic frameworks (MOFs) are crystalline materials composed of metal ions (or metal clusters) and organic linkers [1–5]. As a novel class of porous materials, MOFs have attracted great attention in recent years owing to their high surface area and permanent porosity.

Fig. 1 shows the structures of some reported MOFs. As shown in the figure, MOFs are made by linking inorganic and organic units via strong chemical bonds. The organic units are divalent or polyvalent organic carboxylates, which when linking to metal-containing units (e.g. Zn^{2+} , Co^{2+} , Cu^{2+} , Mg^{2+} , Ni^{2+} , Al^{3+}), can yield architecturally three-dimensional structures with well-defined pore size distributions. The surface area of MOFs typically ranges from 1000 to 10,000 m^2/g , and pore size can be tuned as large as 9.8 nm by altering the organic and metal-containing units [6–9]. As O’Keeffe previously reported, the same metal clusters could be connected by ditopic carboxylate linkers with different lengths to produce a variety of MOFs materials with the same network topology (Fig. 1b) [10]. The variety of constituents’ geometry, size, and functionality has led to more than 20,000 different MOFs being reported and studied within the past few decades [2]. Transition metals (e.g. Zn, Co, Cu, Fe, Ni), alkaline earth elements (e.g. Sr, Ba), p-block elements (e.g. In, Ga), actinides (e.g. U, Th), and even mixed metals have been used for the synthesis of MOFs [11–15]. For example, MOF-5 is commonly based on nets of linked Zn_4O tetrahedrons via 1,4-benzenedicarboxylate (1,4-BDC) ligands, resulting in a three-dimensional cubic network structure with interconnected pores diameter of 12 Å. Moreover, simply changing the metal units from Zn_4O to Cr_3O results in an obvious change in structure from MOF-5 to MIL-101, which contains large cages with the diameter of ~3 nm (Fig. 1) [16]. Since they are comprised of two main components,

MOFs with desired structures can be designed by careful selection of metal centers and different organic ligands [17].

1.2. Nucleation and growth mechanism of MOFs

The most prevailing synthesis methods for MOFs are hydrothermal and solvothermal approaches (Fig. 2) [18], which have reaction times from several hours to days. In a typical solution-based MOFs forming process, a nanoporous material can be formed through a process of nucleation and spreading, and then multiple nucleation aggregate with surface adsorbed organic molecules into an inorganic–organic crystal. To produce controllable nanoscale MOFs crystals and shorten the synthesis time, some alternative synthesis approaches have been attempted, such as microwave-assisted [19–21], sonochemical [22], electrochemical [23], and mechanochemical methods [24].

A key structural feature of MOFs is their high porosity as well as high surface area, which plays a crucial role in their functional properties. Therefore, understanding the molecular forming mechanism of MOFs has been a widely researched topic [25–27]. By in situ observing the MOFs surface features in the process of nucleation and spreading, Moh and co-workers [26] revealed the forming process of Zeolitic Imidazolate Framework-8 (ZIF-8) in 2011. As Fig. 3(l) shows, the nanoporous ZIF-8 occurs through a process of surface nucleation and spreading of successive metastable unenclosed sub-steps in a correlated manner, eventually forming stable surface steps of the enclosed framework structure. After that, Zhou et al. revealed the formation mechanism of MOF-5 [$Zn_4O(C_8H_4O_4)_3$] crystals. It is demonstrated that in the earliest stage, Zn^{2+} and $C_8H_4O_4$ molecules combined with each other and forming crystalline nanoplates with diameter of 5–10 nm. With the assistance of 1,4-BDC molecules, the nanoplates aggregate fast from surface adsorbed organic molecules into layered inorganic–organic microplates. With an increase in reaction time to 6 h or longer, all the microplates further joined together to form loosely

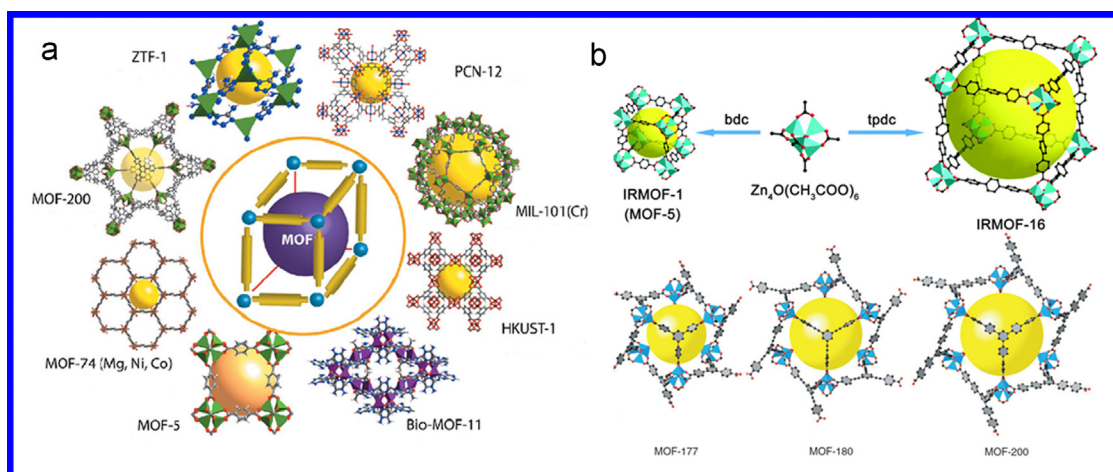


Fig. 1. Schematic representation of reported MOFs structures [3,16].

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