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Review article

Synthesis and applications of MOF-derived porous nanostructures

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Abstract

Metal organic frameworks (MOFs) represent a class of porous material which is formed by strong bonds between metal ions and organic linkers. By careful selection of constituents, MOFs can exhibit very high surface area, large pore volume, and excellent chemical stability. Research on synthesis, structures and properties of various MOFs has shown that they are promising materials for many applications, such as energy storage, gas storage, heterogeneous catalysis and sensing. Apart from direct use, MOFs have also been used as support substrates for nanomaterials or as sacrificial templates/precursors for preparation of various functional nanostructures. In this review, we aim to present the most recent development of MOFs as precursors for the preparation of various nanostructures and their potential applications in energy-related devices and processes. Specifically, this present survey intends to push the boundaries and covers the literatures from the year 2013 to early 2017, on supercapacitors, lithium ion batteries, electrocatalysts, photocatalyst, gas sensing, water treatment, solar cells, and carbon dioxide capture. Finally, an outlook in terms of future challenges and potential prospects towards industrial applications are also discussed.

Keywords: Metal organic frameworks; Porous nanostructures; Supercapacitors; Lithium ion batteries; Heterogeneous catalyst

1. Introduction

1.1. Metal organic frameworks (MOFs)

Porous materials such as porous ceramics, zeolites, activated charcoals, porous metal, polymer foams, and porous glass are being used in many ways in our daily lives. Due to their well-known properties and wide range applications, the field of porous materials, in particular the nanoporous materials, has undergone rapid development in the past two decades. Among the recent developed porous materials, metal organic frameworks (MOFs) are distinct from other traditional porous materials because of their high porosity and thermal stability. Formed by the three-dimensional crystalline assembly of inorganic metal ions and organic ligands, MOFs enable flexible structure design of which well-defined pore sizes, surfaces areas and functionalities can be tailored by selecting different building blocks. This high degree of customizability of MOFs properties has attracted the interest of many researchers. To date, there are more than 20,000 different structures of MOFs being reported and studied [1]. A few examples of different MOFs structures are illustrated in Fig. 1.

Depending on the final structures and properties, MOFs may be prepared using several distinct synthetic methods such as: slow diffusion [3], hydrothermal (solvothermal) [4], electrochemical [5], mechanochemical [6], microwave assisted heating and ultrasound [7]. These synthesis methods and formation

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List of abbreviations

MOFs	Metal organic frameworks
ZIF	Zeolitic imidazolate framework
EDLCs	Electric double-layer capacitors
LIBs	Lithium ion batteries
MWCNTs	Multi-walled carbon nanotubes
TEM	Transmission electron microscopy
NPC	Nitrogen-doped porous carbon
NPM	Non-precious metal
AQ	Anthraquinone
NQ	1,4-napthoquinone
TCBQ	Tetrachlorobenzoquinone
BDC	1,4-benzenedicarboxylic acid
BTC	1,3,5-benzenetricarboxylic acid
NTCDA	1,4,5,8-naphthalenetetracarboxylic dianhydride
PTCDA	Perylene-3,4,9,10-tetracarboxylic dianhydride
MMT	Montmorillonite
RHE	Reversible hydrogen electrode
SCE	Saturated calomel electrode

mechanisms of MOFs have been comprehensively reviewed by Seoane and co-workers recently [8]. A wide range of potential applications of MOFs, ranging from gas (e.g. hydrogen) storage and separation, sensing, catalysis, to drug delivery, has also been reviewed [9,10]. After nearly three decades since the first report on synthesis MOFs [11], a few MOFs are now produced commercially. One of the most prominent commercialized MOFs is Cu-BTC (also known as HKUST-1) produced by BASF (marketed under the trademark BASOLITE® C 300) and sold by Sigma Aldrich [2]. Among other companies which hold patents for large scale synthesis of MOFs are MOF Technologies, Ford Global Technologies, Toyota, and Strem Chemicals. A search on the World Intellectual Property Organization (WIPO) database revealed a constant increment of the number of patents published by the world-wide research community. This indicates that MOFs are gaining a considerable momentum towards commercial applications. The number of patent publications from the years 2007–2017 and the number of patents filed by each country are shown in Figs. 2 and 3, respectively. These patents cover the production and applications of various MOFs or their composites. Fig. 3 also highlights that the top two highest numbers of patents are filed by innovators from United States and China. This is a clear evidence that the researchers from these two countries are committed to the exploration of the commercial opportunities of MOFs. On the other hand, according to the WIPO database, the company which currently owns the highest number of patents is BASF, with 133 patents published so far.

In addition, the huge library of MOFs structures and the optimized synthesis methods are helpful for researchers to explore some other potential applications of MOFs, such as the usage of MOFs as sacrificial materials for the synthesis of various nanostructures. This has opened a new direction in application of MOFs, and might contribute to a better understanding of the properties of porous materials. It is evident that many of the papers published from the years 2008–2013 are short communications or research work focusing on the synthesis of various new nanostructures from MOFs and determination of the basic physical properties of the resultant structures. Very few have measured the performance of these materials against specific applications and study their recyclability. The synthesis method of nanostructures from MOFs has been reviewed thoroughly by Mai et al. [12]. However, to the best of our knowledge, there is not yet a review that is specifically devoted to the synthesis and characterizations of MOFs-derived nanostructures for applications in energy related materials, devices, and processes. For this very reason, we intend to seize this opportunity to review on recent advances in MOF-derived nanostructures for energy-related applications from the years 2013–2017, and to anticipate the prospects of these MOF-derived nanostructures.

1.2. Synthesis of various nanostructures from MOFs

Porous carbon, metals, metal oxides, and their multicomponent hybrids are important inorganic materials for energy and environmental applications. Dependent on the desired application purposes, porous materials can be prepared by several synthetic approaches such as hard templating and soft templating. Hard templating method involves the framework precursors filling the cavities present in the structured solid template of which the template can be removed from the porous structure after synthesis. In comparison, soft templating method involves a more subtle physical or chemical interactions between framework source and template which direct the self-assembly synthesis to allow better control of the material properties [13]. When compared between these two templating approaches, soft templating provides a more successful pathway for the synthesis of ordered and disordered porous matrices [14]. In the soft templating route, porous materials are generally synthesized using the solvothermal method. This solvothermal method is also the most preferred method for large scale production, owing to its relative simplicity and scalability. Aside being used for the synthesis of zeolite, the concept of solvothermal synthesis method has also been applied with great success for the synthesis of MOFs.

In the context of synthesizing various nanostructures from MOFs, MOFs can act as a precursor in which the metal components provide an intrinsic metal source to derive nanostructures of metals or metals oxides, as well as a self-sacrificing template, in which the organic components can be used as a carbon source to prepare nanoporous carbon [15]. In general, certain MOF structures, such as Cu-BTC and MOF-5, are collapsed during the carbonization process, whereas other MOF structures, such as ZIF-8 and ZIF-67, are better in providing a template to guide the formation of pores by allowing evaporation of confined organic moistures during pyrolysis, resulting in a spongy-pore system. Nevertheless, a homogeneous distribution of nanoparticles in their respective