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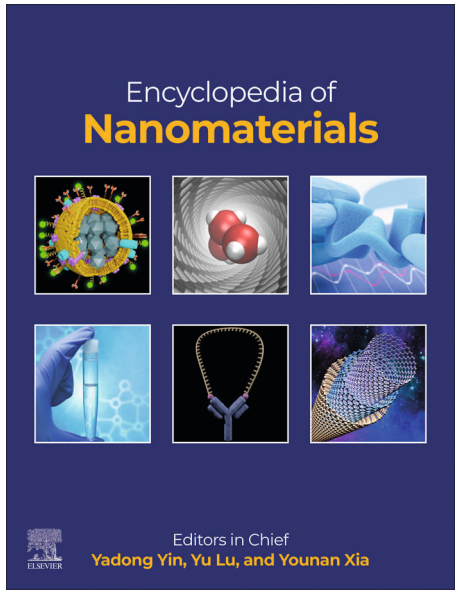

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Shah, Syed Shoaib Ahmad and Jiang, Hai-Long (2023) Functional crystalline porous materials. In: Yadong Yin, Yu Lu and Younan Xia (eds.) *Encyclopedia of Nanomaterials,* vol. 1, pp. 336–354. Oxford: Elsevier.

http://dx.doi.org/10.1016/B978-0-12-822425-0.00070-1

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Functional crystalline porous materials

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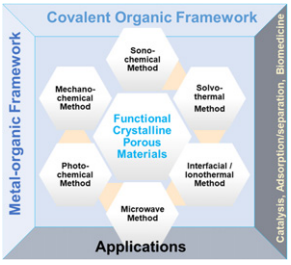
Abstract

In general, the functional crystalline porous materials (CPM) are composed of an ordered structure with distinct molecular spaces for interrelating secondary molecules. In this context, emerging porous and crystalline materials, especially metal-organic frameworks (MOFs) and covalent organic frameworks (COFs) have attracted much attentions for several applications. Thus existing synthetic methods are randomly applied for the large scale production of COFs/MOFs (CPM) and new synthetic strategies are also developed. Herein, we have summarized the synthetic methods for the synthesis of functional crystalline porous materials with recent examples, following the advantages and disadvantages of each method. The possible applications of these materials are also discussed to express the practical viability of these materials and finally future perspectives are provided.

Graphical Abstract



 doi:10.1016/B978-0-12-822425-0.00070-1

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Key Points

- Reticular Chemistry of Crystalline Porous Materials.
- Synthetic Strategies of Crystalline Porous Materials.
- Applications of Crystalline Porous Materials.

Introduction

Porous materials are characterized by pores that include voids, channels or cavities (Cote *et al.*, 2005; Lee *et al.*, 2009; Corma *et al.*, 2010; Yaghi *et al.*, 2003; Furukawa *et al.*, 2010). They are essential for a wide range of applications, from building materials to energy technologies (Davis, 2002; Wu *et al.*, 2012; Su *et al.*, 2013; Jin *et al.*, 2014; Ding and Wang, 2013). The properties of porous materials and their suitability for different applications are closely linked and vary depending on the size, arrangement and shape of the pores, as well as the composition of material itself (Diercks and Yaghi, 2017). Chemists, meanwhile, have shown great interest in the synthesis of porous and crystalline structures by means of chemical science. Crystalline porous materials (CPM) with potential and benefits such as chemical stability, material construction and feasibility of hybridization with other materials are ideal for several applications including catalysis, (Sun *et al.*, 2021; Yang *et al.*, 2021; Wang *et al.*, 2021; Li *et al.*, 2021; Jiao *et al.*, 2021; Wu *et al.*, 2020; Sun *et al.*, 2020; Li *et al.*, 2020a; Jiao *et al.*, 2020a,b) separation, (Yu *et al.*, 2021) gas storage and biomedical. As a result, through ongoing efforts, scientists are moving closer to the coveted aim to control the composition and structure of porous materials, which regulate their function. The foremost advances have been the improvement in flexible assembly, which uses monomers that can be predictably assembled into adjacent subunits Jiang *et al.* (2016). The impulsive emergence of amazing porous materials, such as metal-organic frameworks (MOFs) alleged by coordination bonds (Furukawa *et al.*, 2013) and covalent organic frameworks (COFs), in which carbon atoms and other lightweight elements are covalently bonded to define open networks (Waller *et al.*, 2015). Previously, no material allowed precise and simultaneous control of structure and composition. But the modular nature of these materials allows independent tuning of pore geometry and chemical functionalities (Zhang *et al.*, 2021a; Ding *et al.*, 2019). The environmental friendly and economically viable applications of porous materials in industrial catalysis, adsorption and ion exchange processes have led to efforts to study their fundamental properties and manipulate their structure and functions to improve performance (Zhuang *et al.*, 2019; Wang *et al.*, 2020; Shah *et al.*, 2020a; Nazir *et al.*, 2020; Najam *et al.*, 2021a; Shah *et al.*, 2020b; Aslam *et al.*, 2018; Khan *et al.*, 2020a; Ahmad *et al.*, 2020; Khan *et al.*, 2020b). The custom synthesis of COFs and MOFs makes them ideal candidates for developing structure-property relationships, as well as for addressing current energy and environmental sustainability challenges such as gas storage and separation, catalysis, environmental remediation, and chemical sensing (Zhuang *et al.*, 2019; Wang *et al.*, 2020; Shah *et al.*, 2020b; Ahmad *et al.*, 2020; Qiu *et al.*, 2021).

Crystalline porous materials such as MOFs and COFs have established much more attention and progress in recent years (Qiu *et al.*, 2021; Jiao *et al.*, 2019; Jiao and Jiang, 2019). The individual integration of organic units for the production of prefabricated skeletons with nanopores has resulted in the development of a large number of crystalline materials with different structures. The first family of porous materials consisting of reticular chemistry were metal-organic frameworks (MOFs) that bind polyatomic inorganic complexes containing metals to multiple linkers. The degree of coordination of metal components is combined with the functional diversity of organic part/linker in molecules to create enormous potential. The linking of molecular building blocks by covalent bonds to form extended crystal structures has led to the creation of MOFs and COFs, which allow the accuracy and flexibility of covalent and/or coordination chemistry to be exploited the distinct molecules into stretched structures. An important improvement in this respect has been the improvement in strategies to address the 'problem of crystallization' that often arises when endeavoring to link molecular building blocks into covalent solids. Molecular units interconnected in this way are part of a new environment in which they have (1) lower degrees of freedom, (2) well-defined spatial arrangements, and (3) ordered patterns to which covalent functional groups can be attached to create chemical complexity. The concept of covalent chemistry beyond molecules is extended by the fact that covalent reactions can take place in these structures while their crystallinity and porosity are fully preserved. Following reticular chemistry, in 2005, Yaghi and his colleagues revealed the benefits of the topological design principle in the synthesis of porous organic frameworks associated with covalent bindings, which were the first successful examples of COFs.

In this article, we will use term “crystalline porous materials (CPM)” for both MOFs and COFs and would be rationally defined as “CPM is the polymeric form of crystalline porous materials that allow the integration of organic/ inorganic building blocks into an orderly structure with atomic exactitude”. This groundbreaking research of reticular chemistry, the chemical composition of CPM has been significantly developed and has great potential for functional research. As a nascent with flexible and tunable structure, CPM are emerging materials due to their wide range of applications almost in every field of life.

Design and Synthesis of COFs

COFs symbolize an emergent class of porous crystalline materials consisting exclusively light-weight elements and associated with covalent bonds in two-dimensional and three-dimensional structures (2D and 3D). Subsequently in 2005, the first report (Cote *et al.*, 2005) on COF has achieved a pioneering role in solid-state polymer materials, thanks to their periodic frames, extremely low density, high surface area,

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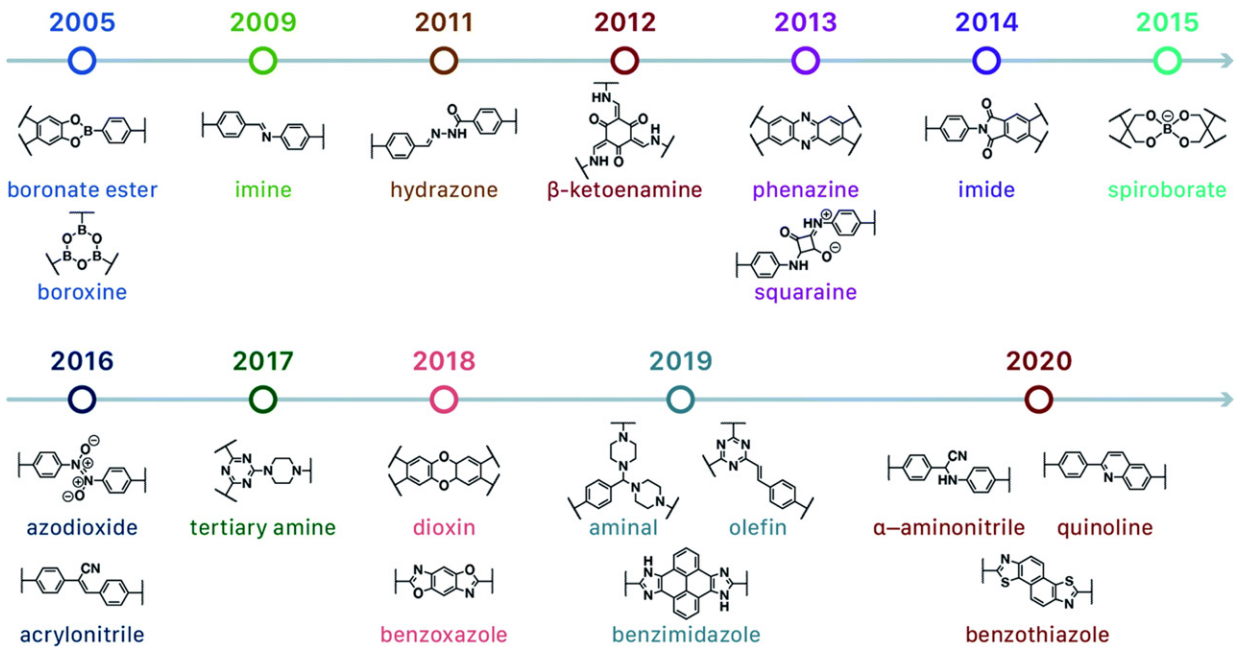

Fig. 1 Common linkages reported for COFs formation. Reproduced from Guan, Q., *et al.*, 2020. Nanoscale covalent organic frameworks as theranostic platforms for oncotherapy: Synthesis, functionalization, and applications. Nanoscale Advances 2 (9), 3656–3733.

courteous topologies and numerous functionalities. The unique set of building blocks is the basis for extensive use in various applications. The synthesis of COF is typically realized by embroidery of organic monomers using dynamic covalent chemistry (Lyle *et al.*, 2019).

A useful aspect of chemistry is the ability to predict structures of COFs based on linkers or combining unites. This structural predictability is mainly due to the possibility that a group or a small number of crystal structures of certain couplings may be generated by their connections. The development of new chemical bonds in the COFs' structure is remained emerging since the 2005 (Guan *et al.*, 2020). Recent researches showed the successful use of conventional irreversible bonds in the formation of COFs because during the fabrication of extended crystalline solids, the bond formation between the monomers is usually reversible and quick reaction rate is essential to proceed the appropriate defects and self-correction, (Guan *et al.*, 2020; Lohse and Bein, 2018) the common linkages used so for in COFs synthesis are shown in **Fig. 1**.

Since numerous COFs chemically separated may have the identical structures, such as eclipsed hexagonal layers, (Cote *et al.*, 2005; Zhang *et al.*, 2021b) topology is used as a language to describe COF according to its compatibility. The topology is usually defined via series of peaks and edges, making a strongly extended structural model independent of chemical identification, geometry, or measurement, provided that the underlying connection between the structures remains the same.

In other words, for unique properties of COF chemistry, the known accuracy of organic chemistry is applied to discrete molecules to reach 2D and 3D structures: (i) the structural composition of these frames maintains its shape in COF formation using geometrically well-defined molecules and comprehends how these molecules are exalted and crystallized; (ii) achieving effective crystallization by carefully examining reaction conditions and selecting the bonding and balance of thermodynamic and dynamic control (iii) COF crystallization and porosity contribute to the chemical transformation of the framework. Synthetic difficulties in obtaining new bonds initially led to dependence on highly reversible condensation reactions such as boroxin anhydride and ester formation, which compensated for the degree of crystallization and chemical stability of the resulting material under hydrolytic conditions, limiting their physical use. A strong interpretation on growth and development of COFs crystals is extremely important because they hold the key to logical construction, synthesis and improvement of new frameworks. For this purpose, an in-depth kinetic study of COF development can provide valued mechanical insights into crystallization processes.

Rational Methods for COF Synthesis

The synthetic strategies can be directly translated into revolutionary results with wide range of applications due to: Supple molecular design and subsequent synthetic strategies, conjugated degree of bending structures, porous properties can be perfectly configured, which showed excellent performance towards several applications. Functional groups in the skeleton/ channels provide effective support and dispersed metallic nodes can work as active sites. Thanks to flexible molecular construction and synthetic strategies, conductivity and activity problems can be resolved correctly by building electron transmission routes between building blocks for electrocatalytic performance. For example, COFs can be integrated with carbon nanotubes or graphene, introduction of active sites, such as metal or functional groups also improved the performance. In addition, due to their heteroatom type, the carbon-containing substances, active catalysts can be derived by using COFs as a precursor. Redox active-sites can

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be easily introduced in flexible structures, which provide a fast kinetics that are essential for the electrochemical process. In addition, equipped with high surface area and regular porous structures, several electrolytes can be kept inside improving their capacity. Further, these regular porous structures are being used for conduction of proton or ions.

Following the pioneering work of Yaghi and his colleagues, there are great efforts to develop various COFs and their applications. Several, synthetic techniques are being used for the synthesis of new COFs with several advantages and disadvantages. Recent studies showed that the morphology and structure of COFs can be modified by altering operative factors under synthetic environments such as solvent, temperature, catalyst and so on. In this context, different compositional approaches have been used for the production of COF. Adjusting the thermodynamic equilibrium in the formation of covalent bond is the key to the formation of arranged covalent networks. The formation of thermodynamically stable crystalline architectures, certain reaction media and conditions (temperature, pressure, presence/ absence of linkers/ templates) are taken into account. For example, mixed solvent/ molten salt systems have been developed for reaction support and microwaves are also used to synthesize COF quickly. In this section we will summarize some emerging methods for COF synthesis and also give a short comparison of advantages and disadvantages of each method.

Solvothermal Method for COF Synthesis

A generally simple way to prepare COF is solvothermal process. The solvothermal method generates COFs by mixing the monomer buildings in a suitable solvent and heating at a specific temperature for defined time interval. The reaction environments depend to a large extent on the solubility and reactivity of the monomers in the solvent as well as on the reversibility of the reactions. Various parameters such as time, temperature, solvent and also the concentration of the catalyst used are important in the morphology and structure of the produced COF. It is worth noting that some COFs can be produced on a large scale using this method.

The monomers and compounds are placed in the pyrex tube and then sealed and heated at a specific temperature for a certain reaction time. The sediments are collected, washed with suitable solvents and dried in the vacuum to form a solid powder. During this process several important factors such as solubility, reactivity of monomers, nucleation/ growth crystal and self-healing of structure are considered when choosing the reaction conditions. For example, El-Kaderi *et al.* (2007) probably produced first 2D COF by using the dioxan and mesitylene (solvents) at 120 °C for 72-hours. The pore size of the produced COF was 6–12 angstrom. Combinations and proportions of solvents are significant elements for the formation and crystallization of the COFs. Combinations of solvents such as dioxan, mesitylene, tetrahydrofuran and Methanol, were used for borate and esters COFs, while a mixture of dioxin-toluene was also used to synthesize COF.

Ionothermal Method for COF Synthesis

In the ionothermal method, ionic liquids or molten salts act as solvents or catalysts and reaction occurs at high temperature. The monomers most commonly used in this method are amorphous materials and lack of extensive molecular order. The use of ionic liquid for COF synthesis makes these methods simple, gentle and green. Zinc chloride was firstly used as appropriate ionic solvent to produce COF by using ionothermal method (Bojdys *et al.*, 2010; Kuhn *et al.*, 2008). Though having a variety of monomers, most CTFs are amorphous materials and do not have extensive molecular arrangement. However, two CTFs, namely CTF-1 and CTF-2, synthesized under ionothermal conditions showed crystalline porous structures. Monomers and $ZnCl_2$ in a pyrex tube are evacuated, sealed and heated at 400 °C for 40 h, followed by stirring in HCl for 15 h to remove Zn-salt. During the synthetic process, molten salt acts as a solvent and catalyzes reaction that is probably reversible at this temperature. This salt-assisted approach is an additional energy-consumable and relatively complex strategy, however, the use of ionic liquid as a solvent provides a simple, mild and green synthetic pathway for 3D COF production (Guan *et al.*, 2018). The 3D series of ionic liquid-assisted COFs (3D-IL-COF) were successfully assembled with 1-butyl-3-methylimidazolium bis((trifluoromethyl)sulfonyl)imide [BMIm, NTf2] as a green solvent and catalyst. In the IL solvent, the tetrahedral building blocks, tetrakis(4-formylphenyl)methane (TFPM), reacts with the linear links of increasing size, p-phenylenediamine (PDA, 6.1 Å), 4,4′-diaminobiphenyl (DABP, 10.7 Å) or 4,4″-diamino-p-terphenyl (DATP, 15.3 Å), to produce the extended 3D interpenetrated **dia** structures, 3D-IL-COF-1, 3D-IL-COF-2 and 3D-IL-COF-3, respectively. The polycondensation continues at ambient temperature and light pressure and can be carried out at a high reaction speed (3 min for 3D-IL-COF-1) (Guan *et al.*, 2018).

Microwave Method for COF Synthesis

The use of microwaves as an alternative energy source in chemistry has been extensively researched in recent years (Nüchter *et al.*, 2004; Wei *et al.*, 2015). This method is considered as superior to solvothermal method due to significantly reducing reaction time and preparation of cleaner products, allowing for a rapid synthesis of COFs (Wei *et al.*, 2015; Diaz de Grenu *et al.*, 2021). Further, microwave synthesis has other assistances, such as possibility of continuous observation and instantaneous checking of chemical reaction conditions. For example, Campbell *et al.* (2009) produced the OF-5 and 3D COF-102 by stirring only for 20 min under MW irradiation at 100 °C, this process was claimed as 200 times faster than conventional solvothermal process. The visualized gray precipitates were revealed as formed COF-5 with a yield of 68%. The MW-assisted synthesis also improves the surface area of COF-5 (SBET- 2019 $m^2 g^{-1}$ $SBET_{(Solvothermal)}$- 1590 $m^2 g^{-1}$) and this increase in surface area was attributed to the removal of impurities by MW process.

Unlike boron-based COF, MW-assisted method was also applied on other linkages and the resulting COF is associated with imine (Wei *et al.*, 2015). Further, porous materials i.e. P1M, P2M and P4M containing covalent triazine framework (CTF) were

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produced using microwave methods (Ren *et al.*, 2012). Initially, the mixture of trifluoromethanesulphonic acid and monomers is sealed in a bottle and kept at 110 °C for stirring for 30 min under microwave, then obtained sediments were ground into powder and washed with ammonia solution. These studies showed a unique feature of MW-assisted synthesis that the oligomers can be efficiently removed and providing a clean COF with more porosity.

Interfacial Method for COF Synthesis

Compared to the other synthetic methods, which mainly lead to insoluble and unconsumed powders complicates or prevents COFs' use several applications such as membrane separation. The interfacial synthetic strategy is a new and effective method to produce fine COF thin films, while controlling their thickness (Dey *et al.*, 2017; Matsumoto *et al.*, 2018; Hao *et al.*, 2018; Wang and Li, 2020).

The basic design principle uses the liquid-liquid or liquid-air interface as a platform and allows simultaneous control of the crystallization and morphology of the framework structure. Thin membranes are grown in free form without any support and can be relocated to the preferred substrate. An important example is the thin film Tp-Bpy, which shows an extraordinary acetonitrile permeance of 339 L m^{-2} h^{-1} bar^{-1}. Tp-Bpy, Tp-Azo, Tp-Ttba and Tp-Tta are dissolved in the interface between two solvents, 1,3,5-triformylphloroglucinol (TFP) in dichloromethane and an aqueous solution of diamine and p-toluenesulfonic acid (PTSA) or water/acetonitrile solution (7/3 in/o) of triamine and PTSA is covered in a dichloromethane layer (**Fig. 2**(a)) (Dey *et al.*, 2017). The interface polymerization of amine and aldehyde monomers was performed with Lewis acid ($Sc(OTf)_3$) catalyzed reaction. The indispensable solutions distinguish the catalyst from the monomers and limit the polymerization at the solution interface (**Fig. 2** (b)). This process provides continuous COF film with a large surface area and thickness of 100 μm to 2.5 nm (Matsumoto *et al.*, 2018). Recently, Suzuki coupling reactions are reported for the synthesis of 2DCCOF1 and 2DCCOF2 with C-C bond formation on a water-toluene interface. The diluted solutions of monomers in toluene and $Pd(PPh_3)_4$ catalyst in the aqueous K_2CO_3 solution were placed in argon at 2 °C and the reactions appeared in the toluene water interface. The solid nanosheets with large surface area of the AB-staggered COF were harvested after 1 month (Zhou *et al.*, 2019).

Sonochemical and Mechanochemical Methods for COF Synthesis

Sonochemical synthetic methods receive a lot of considerations as a substitute way to conventional methods because of economical and fast process (Cintas and Luche, 1999; Bang and Suslick, 2010). This method is also successfully applied for the facile synthesis of COFs, for example, Yang *et al.* prepared COF-1 and COF-5 by using the sonochemical method, COF-1 was produced by the BDBA with a mixture of mesitylene and 1,4-dioxan in an ultrasonic treatment for a single hour (Yang *et al.*, 2012). The ultrasonic treatment supported an effective blend of sparingly soluble BDBA in a mixed solvent system. The COF-1 synthesized by sonochemical method possessed the same surface area but particle size was 400 times smaller than that of prepared by conventional method. COF-5 with BDBA and HHTP was also produced in the same solvent system. Ultrasonic waves not only rush the monomers, but also introduce bubbles that can affect prepared cavities in the COF structure. Oliveira and his colleagues (Oliveira *et al.*, 2020) produced a thin COF film with ultrasonic radiation. The rate of bubble formation can affect the morphology of the prepared COF.

In addition, the sonochemical method allowed the high production of COF-5 and showed more space-time performance than the COF produced with solvothermal process. However, the full potential of sonochemical method has not however been explored, because the synthesis of only few COFs is reported such as boron-based COFs (Li *et al.*, 2020b).

Mechanochemical (MC) method is simple, fast, solvent-free and relatively new technique for COF synthesis, which is carried out at room-temperature only by grounding the reactant/monomers. The mechanochemical method is an economic and ecological that can cover the limits of other methods.

In 2013, Banerjee and co-workers first developed MC strategy to prepare COF without solvents by simply grinding the monomers (TpPa-1(MC) and TpPa-2(MC)) at room temperature for 40 min. The resulting COF showed excellent chemical stability, however, crystallinity and BET surface area was reduced (Biswal *et al.*, 2013). In order to fully exploit the potential of the composition, MC has developed a liquid-assisted grinding approach (LAG) (Das *et al.*, 2014). LAG needs a catalytic amount of liquid to assist reactivity of precursors, therefore, enhanced the production and crystallinity of COF. This method allowed rapid COF synthesis with various monomers, including β-ketoenamine, hydrazine and imine, more rapid as compared conventional method. By using this strategy, Banerjee and his colleagues prepared bipyridine-based COF (Tp-Bpy-MC) at room temperature at 90 min (Shinde *et al.*, 2016). Due to ease of use and an almost reliable process, this strategy is seen as a competitive and sustainable synthetic way for an integrated COF synthesis. In 2017, Banerjee and his colleagues reported a rapid and universal synthesis of MC 2D COF compared to 2 ketoenamine (a total of 12) with p-toluenulfenic acid monohydrate ((PTSA) H_2O) having extremely large surface area (3109 m^2 g^{-1}). The simple procedure is suitable for large-scale fabrication of high quality COFs (approximately 10 g h^{-1}) and COFs with the required shapes. It should be noted that MC method for COF synthesis has so far been shown mainly in ketoenamine-related 2D-COFs and that it is required to generalize it for other linkage-based COF synthesis.

Photochemical Method for COF Synthesis

Photochemical method to synthesize the COFs has developed as an effective methodology to differentiate functional materials (Pietrobon and Kitaev, 2008; Balan *et al.*, 2017). The first synthesis protocol was reported by Kim et.al., in 2017 for

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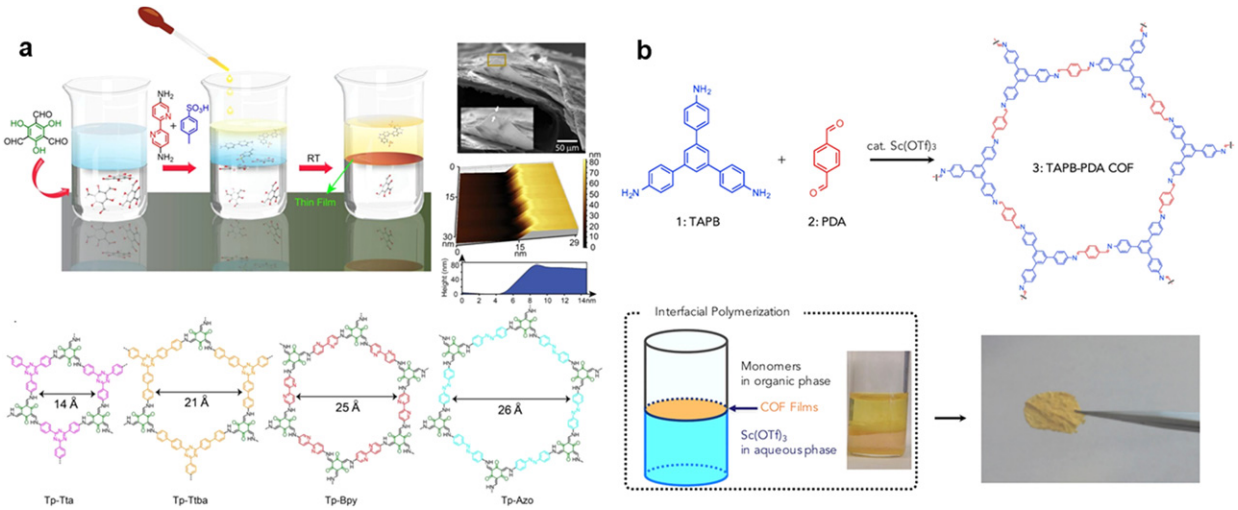

Fig. 2 (a) Interfacial synthesis of COFs, (a) Graphical illustration of synthesis process, SEM/AFM images of Tp-Bpy thin films and chemdraw structures of COFs synthesized by this method. (b) Chemical reaction scheme of COFs, presentation of the interface of the organic phase and aqueous phase, and digital photo of free-standing film. Reproduced from (a) Dey, K., *et al.*, 2017. Selective molecular separation by interfacially crystallized covalent organic framework thin films. Journal of the American Chemical Society 139 (37), 13083–13091. (b) Matsumoto, M., *et al.*, 2018. Lewis-acid-catalyzed interfacial polymerization of covalent organic framework films. Chem 4 (2), 308–317.

the synthesis of COF-5 (UV-COF-5) by ultraviolet radiation (Kim *et al.*, 2017). UV-COF-5 exhibited a better reaction rate of 48-fold as compared to conventional synthesis of COF-5, and high BET surface area (2027 $m^2 g^{-1}$). In particular, UV radiation increased the growth of UV-COF-5 in one direction [001], probably due to a change caused by UV radiation in an intermediate orbital coupling layer, and this fact was further confirmed by DFT studies. Choi and his colleagues further applied this approach and rapid formation of pyrazine-fused COF (hcc-COF) was occurred (Kim and Choi, 2019). The hcc-COF was produced with irradiation of simulated sun-light (200–2500 nm) during three hours at room temperature. The same monomers in the absence of light produced only amorphous polymer, which emphasize that light radiations have a fundamental role. The enormous electrical conductivity of hcc-COF (2.22×10^{-3} S m^{-1}) is attributed to the extended conjugated structure, which assists charge transfer.

Metal-Organic Frameworks

Metal-Organic Frameworks (MOFs), also known as porous coordination polymers, are a class of compounds with mesh structures formed by the self-assembly of metal ions or clusters of metals with multi-dentate organic ligands containing oxygen, nitrogen, etc (Jiao *et al.*, 2021; Zhang *et al.*, 2021c; Liu *et al.*, 2021). The metal ions or clusters of MOFs and the variety of organic ligands, and the diversity of linking approaches between metals and ligands, make MOFs having the advantages of traditional inorganic materials, such as ultra-high surface area and porosity, lower density, pore size and structural flexibility. These unique properties give MOFs potential applications in the fields of gas storage/ separation, catalysis, sensing, proton conductors, and biomedicine (Sun *et al.*, 2020; Li *et al.*, 2020a; Lin *et al.*, 2020; Chen *et al.*, 2020).

Compared with the traditional inorganic compounds, the preparation and structural assignation of MOFs has attracted much attention in recent years (Jiao *et al.*, 2019). MOFs, because of their structural flexibility and highly porous surface area have a wide range of applications and have rapidly developed in the field of porous materials research. Therefore, emerging methods are introduced/utilized for the synthesis of MOFs with high porosity and surface area (Ding *et al.*, 2019). At present, the research on MOFs mainly focuses on the following aspects: MOFs preparation methods and formation mechanism; herein summarized some classic documents on the preparation, shape control and self-assembly of MOFs in recent years, provide reference for the preparation of MOFs with controllable structure, porosity and surface area, and finally introduced the application. In general monomers of MOFs are directly linked to topological structures and spatial diversity of MOFs is translated by these structural advantages. This network of topologies consists of several topological structures (**Fig. 3**(a,b)) including squares, triangles and lozenges (Bhatt *et al.*, 2020).

Synthesis Methods

In the preparation of MOFs, different synthesis methods and experimental conditions have an effect on the coupling of metals and organic compounds, the growth of crystal nucleation, and the self-assembly process, resulting in different structures and shapes. The

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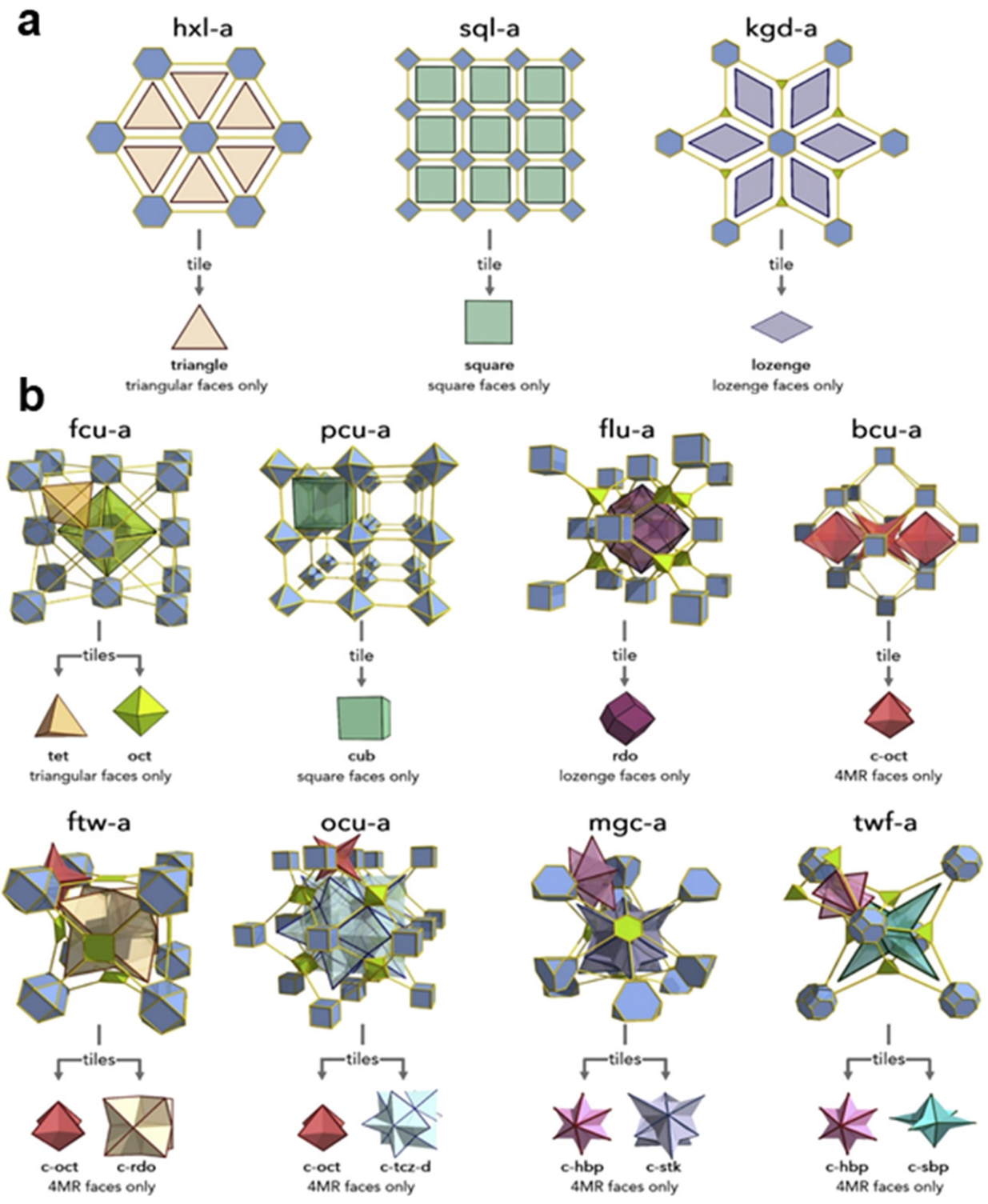

Fig. 3 Amplified presentations and Tiling of the Edge- and Face-Transitive Nets with faces of prime interest, (a) 2D topologies and representatives faces, (b) 3D topologies and representative faces. Reproduced from Bhatt, P.M., *et al.*, 2020. Topology meets reticular chemistry for chemical separations: MOFs as a case study. Chem 6(7), 1613–1633.

energy is usually introduced by conventional electric heating, i.e. the heat is transferred from a hot spring or oven. Alternatively, energy can be introduced in other ways, such as electrical potential, electromagnetic radiation, ultrasound waves or mechanical (grinding) (Shen *et al.*, 2005a,b; Jiang and Mao 2006a,b; Jiang *et al.*, 2006; Jiang *et al.*, 2010b; Jiang and Xu, 2010; Liu *et al.*, 2010; Aranishi *et al.*, 2011; Gu *et al.*, 2011; Jiang *et al.*, 2011b). The duration of reaction, pressure and energy of the molecule introduced

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into the system are main factors which are closely related to energy source and individually affect the topology/morphology (Aranishi *et al.*, 2011; Gu *et al.*, 2011; Jiang *et al.*, 2011b; Jiang *et al.*, 2007b,c,a; Li *et al.*, 2007; Jiang *et al.*, 2008a,b; Jiang *et al.*, 2011a,c).

Of course, different methods can lead to the specific chemical bonding resulting in different topological structures that otherwise cannot be made (Mao *et al.*, 2008; Jiang *et al.*, 2009a; Zhang *et al.*, 2009; Jiang *et al.*, 2010c,d,a). In addition, other methods may produce the MOFs with different morphologies, surface area and/or particle size that can affect the other properties of materials (Aranishi *et al.*, 2011; Gu *et al.*, 2011; Jiang *et al.*, 2011a,c; Jiang *et al.*, 2009b; Jiang *et al.*, 2011d; Jiang and Xu 2011a,b; Lan *et al.*, 2011; Feng *et al.*, 2012). For instance, the porous materials with different particle size showed different distribution of guest molecules, which directly affects catalytic reactions or adsorption and separation process (Jiang *et al.*, 2012; Lan *et al.*, 2012a,b; Lu *et al.*, 2012; Feng *et al.*, 2013a, b; Jiang *et al.*, 2013b; Wei *et al.*, 2013; Hu *et al.*, 2014; Li *et al.*, 2014; Shen *et al.*, 2014; Yang *et al.*, 2014; Zhang *et al.*, 2014a,b,c,d,e; Zhou *et al.*, 2014). Nanocrystalline, non-toxic high-load carriers are also considered for biomedical applications (Keskin and Kızılel, 2011; Shah *et al.*, 2018). For this purpose, sonochemical and microwave methods were used. Instead, larger individual crystals (in the range of 100 μm) are required to systematically regulate the structure and create relationships of structural properties.

For the commercialization of MOFs, it is highly required to create simple, affordable, fast and cost-effective method for MOF synthesis. The reaction time and temperature are the most common factors for controlling the cost of reaction, for this quick reactions may be the beneficial for large scale production. Numerous recent surveys assessed the impact of synthetic route on the formulation of the MOFs. Some other variable are also the main criteria of these studies including the rate of crystallization, size of particle, surface area and adsorption properties (Remya and Kurian, 2019; Zhou and Kitagawa, 2014). The problematic fact associated with synthesis of MOFs is a comprehensive characterization of all materials with additional characterization methods is imperative, as even minor change in procedure may result in the combination of extremely different properties (Hafizovic *et al.*, 2007; Kaye *et al.*, 2007).

Herein, we described various synthetic protocols in which energy is introduced by different sources and discussed the effects of experimental conditions on product structure, size, appearance and crystallization.

Solvothermal or Conventional Method

This method is the most common method for the preparation of MOFs, which mixes metal salts, organic ligands, water or organic solvents and reacts under certain temperature and pressure conditions for a period of time to obtain the final product. The term conventional method (synthesis) is usually applied to reactions carried out by conventional electrical heating i.e. the reaction temperature is one of the main parameters of MOF synthesis and usually two temperature ranges are distinguished; solvothermal and non-solvothermal, which determine the type of reaction settings to be applied. Although no common definition of solvothermal reactions is defined, we used the Rabenau's statement,(Rabenau, 1985) "reactions that take place in closed containers under autogenous pressure above the boiling point of the solvent". As a result, non-solvothermal reactions occurred under/ at boiling point and atmospheric pressure, simplifying synthetic requirements. Non-solvothermal reactions can be further classified as reactions to room temperature or reactions that occur at elevated temperatures.

The early work was mainly based on low-temperature synthesis methods and a precipitation reaction was reported, followed by crystallization or slow evaporation of the solvent. These methods are known for the development of simple molecular or ionic crystals, as it is possible to perfect reaction conditions, i.e., the speed of nuclei and the development of crystals. When developing crystals from clear solutions, the concentration of reaction agents should be adjusted to exceed the critical concentration. This is usually achieved by changing the temperature or evaporation of the solvent. Methods such as evaporation of the solvent, layering of solutions or slow concentrations enhanced the gradients that allow MOF precipitation and this can also be achieved by using the temperature as a variable.

Some important MOFs were synthesized by simple mixing of metal-salts and ligands at room temperature with appropriate solvent, for example MOF-5, MOF-74, MOF-177, HKUST-1, ZIF-67 and ZIF-8 (Cravillon *et al.*, 2009; Huang *et al.*, 2003; Tranchemontagne *et al.*, 2008). This synthesis method can also be referred as an immediate precipitation reaction and illustrates that the crystallization of a MOF takes place in short time. Some of these MOFs, such as ZIF-8, show surprisingly good thermal and chemical capabilities. Fluctuations in temperature during the reaction process have also influence on the formation of product and concentrated structures are often detected at higher temperatures. However, the high temperature, in some cases, is also compulsory to achieve the correct crystallization and reaction speed, especially when using kinetically inert reactants. The reaction temperature also has an effect on crystal morphology, however, MOF are subjected to degrade during long reaction time (Millange *et al.*, 2011). The vast majority of MOFs can be prepared by solvothermal method, such as MOFs with Fe-MIL (Material of Institute Lavoisier) series, and MOFs with Zn, such as MOF-74 and UiO (University of Oslo) series (Winarta *et al.*, 2020; Gao *et al.*, 2021).

During the preparation process, the reaction temperature and time, pH and the molar ratio of the metal and the ligands have a great influence on the crystal-structure, size and morphology of MOFs, and often can be controlled by changing these experimental parameters. In addition, since additives can combine with metal ions or compete with ligands to control the nucleation and growth rate of MOFs, the introduction of additives can also regulate the shape and size of the product. For example, in the preparation of the MIL series of MOFs, the additives can be added in conjunction with Fe (III) to prevent the distribution of organic ligands and Fe (III) to control the growth of MOFs' particle size.

Although solvothermal method is still a common method for preparing MOFs, and can control the size and appearance of MOFs particles by changing experimental parameters or introducing additives, this method has a relatively long preparation cycle,

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sometimes as long as 1–3 days, and often needs to be carried out under high temperature and high pressure conditions. Therefore, inefficiency, high energy consumption and poor safety are the disadvantages of this method.

Microwave Method

Microwave (MW) synthesis is based on the interaction of electromagnetic waves with polar solvent molecules/ions in the solution or electrons/ions in a solid body. Thanks to the direct interaction of radiation with solution/reaction agents, heating using MW is a very energy-efficient heating method. Microwave synthesis of MOFs, through radiation energy transfer, provides MOFs materials with rapid nucleation, so that MOFs can be quickly crystallized. In the solution, polar molecules try to align in an electromagnetic field and in an oscillating field so that the molecules change orientation permanently. Thus, when the corresponding frequency is used, the molecular collisions are responsible for increasing the kinetic energy of the system. The choice of appropriate solvents and selective energy intake must be taken into account, since the starting materials can interact strongly with MW radiation.

MW-assisted MOF synthesis focused primarily on (1) acceleration of crystallization, (2) to improve product purity and selectivity. For example, IRMOFs or some others require 48–100 h to be prepared using traditional solvent thermal systems, while when microwave heating is used, IRMOF-1, IRMOF-2, and IRMOF-3 can be obtained in just seconds (Ni and Masel, 2006; Kim *et al.*, 2011; Mai and Liu, 2019).

Several MOFs with carboxylic acid ligands (M = Fe, Al, Cr, V, Ce) were produced with a MW-assisted composition. The first MW-assisted synthesis of MOF was probably MIL-100(Cr) and was synthesized during MW irradiation with a yield of 44% in 4 h at 220 °C (Jhung *et al.*, 2005). The analog MOF having Fe as metal center was detected in 30 min in a 200 °C. Further studies showed that nanoparticle size was increased from 40 to 80–70–90 nm and nanoparticles of homogeneous size were obtained by increasing time of reaction during synthesis of Cr-MIL-101 (Jhung *et al.*, 2007). The following report prevented the use of HF and Cr-MIL-101 nanocrystals (50 nm) with a yield of 37% was obtained by reducing reaction concentration or increasing the pH of the reaction mixture (Khan *et al.*, 2011). However, the particle size was not affected by the reaction time. Fe-MIL-101 nanocrystals with an average diameter of 200 nm were associated with DMF as a solvent at 150 °C in 10 min (Taylor-Pashow *et al.*, 2009) and only a small amount of BDC-NH_2 was included in nanocrystals. The following report, Horcajada *et al.* (2010) produced 173 ± 60 nm octahedral nanocrystals containing only BDC-NH_2 in water at 60 °C in 5 min. In a systematic study showing the effect of synthesis and parameters on the formation of the Fe-MIL-88A, only MW-based hydrothermal synthesis ensured rapid synthesis of small nanoparticles (<100 nm) and highly effective single-use dispersions Chalati *et al.* (2011a). An ex situ and in situ time-differentiated crystallization studies were carried out which showed that irradiation of MW resulted in a faster reaction rate than heating during synthesis of Fe-MIL-53 (Haque *et al.*, 2010) and CAU-1$(OH)_2$ (Ahnfeldt *et al.*, 2011). These studies illustrated that MW-assisted synthesis is a benign and fast route for preparation of functional materials, avoiding the use of toxic reactants/solvents. For example, synthesis of MIL-101(Cr), there is no need to add strong corrosive HF. Similarly, using water and ethanol as solvents, MIL-100 (Al, Cr, Fe) can be prepared through microwave systems, with yields of more than 90% and no more toxic solvents such as DMF are used. Since microwave heating does not need to pass through the container to transfer heat, it can greatly increase the rate of heating and reduce the loss of heat in the conduction process, so the use of microwave heating can significantly shorten the time required for sample formation, and reduce the amount of solvent. The disadvantage of this method is that the reaction is too fast, the nucleation and growth speed of the crystal is difficult to control, so the preparation of the product size uniformity is poor.

Ultrasonic Method

Like the effect of MW irradiation, ultrasonic (US) irradiation is also alternative method which contributes to fine synthesis of various materials (Majewski *et al.*, 2018). US method also increases nucleation rate and ultimately nano-sized MOF particles are obtained, mainly due to the increase in local high temperature and pressure and the resulting collapse of acoustic cavitation (Khan and Jhung, 2015), Qiu *et al.* (2008). used this method (US-assisted) for the synthesis of nanoscale MOF (Zn_3(btc)$_2$–12 H_2O) (btc = 1,3,5-benzenecarboxylic acid) and nanosized crystals (50–100 nm) were formed after 10 min of US irradiation (40 kHz) and 60 W power at room temperature. In this study, it was also found that the size of the crystals increased sharply between 700 and 900 nm when the irradiation time was extended by 90 min. These results clearly show that the morphology of nano-sized MOFs can be controlled by varying the ultrasound time. MOF-177 microcrystals with the size of 5–20 μm were synthesized by US irradiation within 40 min at 500 W (Jung *et al.*, 2010). These reports clearly show that US irradiation is an effective technique for MOF synthesis. Since then, several studies reported the synthesis of MOFs via US-assisted method to control the size, morphology of nano-MOFs (Bux *et al.*, 2009; Bigdeli and Morsali, 2015; Carson *et al.*, 2011).

The studies showed radiations supported procedures meaningfully reduced time of synthesis, which in most cases was only a few minutes, in contrast to classical methods such as solvothermal method usually requires some hours to days.

Co-precipitation Method

Co-precipitation method is one of the common methods used to prepare MOFs, the principle of which is mainly to make MOFs precipitate quickly by introducing depraved solvents. According to the addition time of the bad solvent is subdivided into 2

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synthesis methods: (1) the bad solvent is used as the initial solution of the reaction, and the resulting MOFs are insoluble in the reaction solution, thus presuming the product;.

The advantage of co-precipitation method is that the reaction speed is fast, can be used for batch preparation products, the disadvantage is that this method is not universal, only suitable for synthesis of some of the more easily synthesized MOFs at room temperature, such as HKUST, ZIF-8 and so on.

Mechanochemical Method

Mechanochemical method is the solvent free protocol for MOF synthesis in which bulk reactor chemical reactivity is achieved by applying mechanical force (Pichon *et al.*, 2006). Microporous MOFs can be easily obtained by this technique environment friendly and scalable method due to the nominal usage of solvents. Further, this method enables the easy fabrication of smaller nano-sized MOFs by subjecting the material to natural grinding conditions, which results in small pieces. The microporous copper(II) isonicotinate MOF crystals (size $<$ 100 nm) were first attained by grinding a mixture of copper(II) acetate and isonicotinic acid powder for 10 min (Pichon *et al.*, 2006). The same approach was used for the synthesis of general MOFs including HKUST-1 (Klimakow *et al.*, 2010).

The milling of a mixture of metal salts and organic ligands is relatively unusual, but it's a simple, convenient and efficient method to produce nanoscale MOFs. The process is fast and productive and scalable due to its solvent-free nature and time efficacy than solvothermal process. This method also performed better because of several hazardous effects of organic solvents (Bian *et al.*, 2015; Wang *et al.*, 2013). However, this approach must take into account the completeness of the reaction, the preservation of the initial MOF pore parameters (size, shape and distribution) and ensuring constant mechanical strength throughout the reaction mixture (Bian *et al.*, 2015; Vallet-Regí *et al.*, 2007). Similarly, the consistency of the size and shape of the resulting crystals varies significantly with respect to the strength and length of the grinding, which poses a problem for the reproducibility of this technique.

Micro-Emulsion Method

Micro-emulsions are thermodynamic, stable transparent or translucent collision dispersion systems consisting of water, oil and surfactants, usually at the nanoscale or micron level (Jin *et al.*, 2002). The basic principle of micro-emulsion method is that the two solvents that are insoluble form a uniform small droplet under the effect of surfactants, which can be used as limit reaction generators for MOFs. During the reaction, metal ions and organic compounds react at the droplet interface, and then the MOFs product is extracted. The whole nucleation, growth, and extraction process is limited to a small droplet, so compared with other methods, micro-emulsion method has the advantage of accurately regulating MOFs size and appearance. In 2000, Vaucher *et al.* (2000) used micro-emulsions for the first time in the preparation of MOFs and successfully prepared Prussian blue nanoparticles with a particle size of less than 100 nm using a water-anionic surfactant (sodium bis(2-ethylhexyl)sulfosuccinate).

During the synthesis of MOFs, the surfactants are used as capping agents to reduce the aggregation through the nucleation process. Hence, by controlling the nycleation in the surfactants micelles the required size and morphology of the resultant MOF can be achieved (Nikoobakht and El-Sayed, 2001; Jiang *et al.*, 2013a).

A widely used strategy is stabilization with cetyltrimethylammonium bromide (CTAB) (Rieter *et al.*, 2006; Xu *et al.*, 2012; Liu *et al.*, 2012). A prime example for using CTAB has been effectively confirmed in the shrinking of HKUT-1crystal size (Liu *et al.*, 2012). Cubic crystals (6 {100} facets) of HKUST-1 with size of 300 nm were tuned during solvothermal synthesis with CTAB; by increasing the concentration of CTAB to 0.005 M, 0.01 M, 0.05 M and 0.1 M, the particle morphology changed to truncated cubes, cuboctahedrons (400 nm), truncated octahedrons (500 nm) and octahedral (1 μm) respectively. The results indicate that with increasing concentration of CTAB, an evolution of particle morphology is observed and the same time, the particle size was found to increase simultaneously (Liu *et al.*, 2012). Further, accurate control of morphology was achieved by using the MOF-5 formulation at room temperature (Yuan *et al.*, 2011). By using the surfactant, rod-shaped crystals (200–500 nm) of MOF-5 were ensued, a width of 50–100 nm and a thickness of 50–80 nm, whereas surfactant-free synthesis produced unbalanced morphology with large size crystals 1–2 μm (Yuan *et al.*, 2011).

Lin and others extended the micro-emulsion method to the preparation of other MOFs, and studied the molar ratio of water and surfactants and the effect of temperature on MOFs morphological appearance (Rieter *et al.*, 2006; Taylor *et al.*, 2008). They prepared the micro-emulsions of the metal Gd and BDC in the CTAB-isooctane-hexanol-water system, respectively, and then mixed the two at room temperature to obtain the product. By adjusting the reaction concentration and parameters such as molar ratio of water and surfactant CTAB, a different size of rod $Gd(BDC)_{1.5}(H_2O)_2$: by varying the molar ratios, nanorods of 100–125 nm with a width of 40 nm, and microbars with a length of 1–2 μm and a width of 100 nm are obtained (Rieter *et al.*, 2006).

The effect of surfactant dosage was also studied in two different MOFs, (Xu *et al.*, 2012; Liu *et al.*, 2012) nanoparticles are prepared with micro-emulsions, the product size can be adjusted by adjusting the amount of the surfactant (CTAB). In general, micro-emulsion method needs to introduce a large number of surfactants, which are very easy to adsorption in the MOFs material holes difficult to remove, which will reduce the MOFs surface area and adsorption capacity. In addition, this method is not universal, only suitable for the preparation of some of the easier preparation of MOFs.

It should be emphasized here that the current methods for the preparation of micro-nano MOFs have more or less shortcomings and shortcomings, such as the method is not universal, product preparation cycle is long, product shape size uniformity is

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poor, so to find a can be prepared size uniform, shape controllable, with complex structure and shape of the general preparation method of micro-nano MOFs is still extremely challenging.

MOF and COFs Composites

Due to the high demand for fabricating multifunctional catalysts, MOF and COF-based materials are becoming desirable candidates towards high-performance applications. Therefore, continuous research has been paved to incorporate MOFs and COFs with unique characteristics (Dong *et al.*, 2020; Dinari and Jamshidian, 2021). Currently, it is undisputed that the development of MOFs-COFs composite is one of the easiest and highly effective way for developing multiplicity as well as the characteristics of porous framework. Though, tremendous effort has been devoted on the progress of MOFs-COFs composites but still many challenges need to be address. The synthesis and application of MOFs-COFs composites systematically presented the evolution of MOFs-COFs composites from synthesis of individual to combined materials for several applications. This infant field of MOFs-COFs composites will explore the way for the improvement of advanced functional materials based on MOFs/COFs.

The composites based on MOF and COF can be broadly classified as composite based on MOFs or COF, depending on the differences in the substrate for nucleation. MOF-based composites used MOF as the substrate for COF growth for MOF-COF and vice versa. Herein, MOF-COF composites based on MOFs are represented as MOF@COF, while COF-based composites are denoted as COF@MOF.

Due to this desirable diversity, MOFs and COFs are capable of forming different hierarchical structures of MOFs and COFs. Therefore, the fabrication of MOF@COF composites is mostly achieved via adding MOFs or functionalized MOF crystals during COF synthesis route (Peng *et al.*, 2018; Sun *et al.*, 2018; Cai *et al.*, 2019; Garzón-Tovar *et al.*, 2019). Firstly, Zhang *et al.* described the MOF@COF core-shell hybrids (NH_2-MIL-68 @TPA-COF) via utilizing NH_2-MIL-68 as a core-shell substrate followed by functionalization with tris(4-formylphenyl)amine (TFPA) for successive covalent condensation of TFPA and tris(4-aminophenyl) amine (TAPA) (Peng *et al.*, 2018). Notably, the direct utilization of NH_2-MIL-68 as seed is unable to form NH_2-MIL-68@TPA-COF, except for the functionalization with TFPA aldehyde, and the above synthesis approach is also appropriate for MIL-69@TPA-COF fabrication. In view of above results, the MOF-COF amalgamation will produce incredible configurations together with pronounced influence on the properties that will provide a concrete basis towards various applications. Further, Sun *et al.* (2018) stated the preparation of MOF@COF core-shell composites by using MIL-125(Ti) and COF-LZU1. In contrast to a previous report, -NH_2 in MIL-125(Ti) MOFs allowed direct growth of LZU1 via MIL-125(Ti) MOFs addition at room temperature in LZU1 precursors.

With the continuous growth of MOF@COF composites, analogous COF@MOF composites are progressively attracting the attention of researchers. Fu *et al.* described COF-MOF composite membrane via COF-300-coated SiO_2 slice introduction into the mother liquor of $Zn_2(bdc)_2(dabco)$ and ZIF-8 for the synthesis of [COF-300]-[$Zn_2(bdc)_2(dabco)$] and [(COF-300)-(ZIF-8)] composite membrane, respectively, which provides an opportunity for the advanced design of COF@MOF composites (Fu *et al.*, 2016).

In recent time, Feng *et al.* stated a series of COF@MOF composites via introducing COF seeds to MOF precursors (Feng *et al.*, 2020). The highly stable COF-303 was used as a modular scaffold to synthesize COF-303@MOF-5 composites. Further, stability is a known crucial aspect in ensuring the reliability of COF@MOF composites during synthesis process, and it was found that COF-303 microforms are sufficiently stable to survive the UiO-67 synthesis. This ensured the feasibility and ubiquity of this COF@MOF fabrication strategy. Furthermore, the proposed method can also be used to fabricate more advanced three-module COF@MOF other structures (Feng *et al.*, 2020). This overall flexible synthesis approach can not only extend the range of COF@MOF composites but also construct efficient porous frameworks with unlimited synergy, design and precision.

Applications of CPM

CPM materials (MOFs and MOFs) have potential application prospects in catalysis, gas storage, sensing, proton conductors, biomedicine, etc. due to small size and the advantages of matching unsaturated metal bits, adjustable aperture and super-high surface area (Jiang *et al.*, 2010d; Jiang and Xu, 2011b). As there are more relevant reviews, it is no longer repeated here, just a few representative examples to give a brief introduction to their application.

Catalysis

Catalysis is one of the more rapidly growing application and CPM (MOFs/ COFs) themselves act as the active part of the catalyst. The metal ions in the skeleton (MOF) provide a high density, uniform dispersion of the active sites for the catalytic reaction, and the great aperture and pore capacity also ensure more full contact between the active sites of the catalyst and the substrate (Shah *et al.*, 2021; Nazir *et al.*, 2021a,b; Najam *et al.*, 2021b; Najam *et al.*, 2020a,b). As a result, CPMs combine the two advantages of homogeneous and heterogeneous catalysts, namely the efficiency of catalytic reactions and the recyclability of catalysts. Compared with ordinary hetero-phase catalysts, the shape and size of pores can be adjusted by changing the organic complement of CPM,

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thus selectively catalyzing substrates of different sizes (Jiang *et al.*, 2009a). In addition, CPMs can also be used as a carrier of the compound catalysts, the catalytic activity of the component loaded in/on the CPMs, can make the active components of the active sites fully exposed and ensured that the compound catalyst has a higher stability (Wang *et al.*, 2021; Jiang *et al.*, 2009b).

For example, recently, Wang *et al.* (2021) reported a facile synthetic strategy to support the encapsulation of octahedral Cu_2O nanocrystals (NCs) by MOFs, and controlled growth of HKUST-1 around Cu_2O NCs is succeeded. After the reduction of Cu_2O into Cu NCs, the Cu@HKUT-1 was fabricated having controlled thickness and uniform morphology (**Fig. 4**(a,b)). The integrated Cu NCs with MOF showed multifunctional catalytic performance and displayed cooperative enhanced performance for one-pot cascade reactions under mild conditions. The better performance is attributed to the photothermal effect and hydrogenation activity of Cu NCs and the MOF shell affords Lewis acid sites. Furthermore, the protective MOF shell in Cu@HKUST-1 guarantees its better recyclability than that of Cu/HKUST-1, in which the MOF particles loaded on Cu NCs easily fall off during reaction. The microenvironment tuning of active sites is considered as emerging strategy to enhance the catalytic performance. The regulation of interaction between the metal nanoparticles and substrate is also a great challenge. Li *et al.* (2021) reported the MOF-encapsulated Pd nanoparticles (Pd@MIL-102-NH_2) and Pd microenvironment was regulated by post-synthetic modifications of $-NH_2$ with perfluoroalkyls (hydrophobic). This post-synthetic engineering improved the substrate enrichment and interaction between the Pd nanoparticles and modified host (MOF), this engineered microenvironment showed better activity and selectivity for the dehydrogenation of organosilane as well as the hydrogenation of nitrobenzenes (Li *et al.*, 2021).

The selective hydrogenation reactions have great importance, but classical Lindlar catalyst showed partially catalytic poisoning and usually Pd-based bimetallic catalysts showed better potential. For example, simulation studies proved the CuPd a promising catalyst for hydrogenation reactions (Kruppe *et al.*, 2017; Cao *et al.*, 2014) but high pressure (H_2) is usually required at experimental conditions (Pei *et al.*, 2017). To overcome this issue, Li *et al.* Li *et al.* (2020a) reported a facile strategy to encapsulate the bimetallic nanoparticles into MOF-structure (CuPd@ZIF-8). The appropriate porous structure of MOF not only inhibit the oxidation of Cu nanoparticles but also provide the substrate-enrichment for inherent localized surface Plasmon resonance of Cu catalysts resulting into the conversion of solar energy into kinetic energy. Further, MOF-shell provide the stability towards core nanoparticles (CuPd) and also offers regioselectivity by the steric hindrance, finally, enhanced the semihydrogenation of alkynes $5–10^5$ times with ammonia borane assisted hydrogenation reaction under visible-light irradiation at ambient temperature (**Fig. 4**(c-e)).

Further, the intrinsic interfacial energy barriers usually restrict the nucleation of metal chalcogenides on the surface of MOFs during synthesis (Chen *et al.*, 2017). For example, the anisotropic growth properties associated with different materials initiate this barrier and confines the assembling of MOF and metal-sulfides (Chen *et al.*, 2017; Shen *et al.*, 2018) Lin *et al.* (2020) reported the controllable and precise growth of metal-sulfides on the MOF surface. A cysteamine supported method was adopted to assemble the metal-sulfides (Cds, ZnS, CuS and Ag_2S) on the unsaturated metal sites in the MOF. The cysteamine acted as a molecular linker and joined the unsaturated sites of MOFs and metal ions via chelating of amine and thiol groups respectively, finally, improving the interfacial interactions between the metal ions and MOF. enhancing

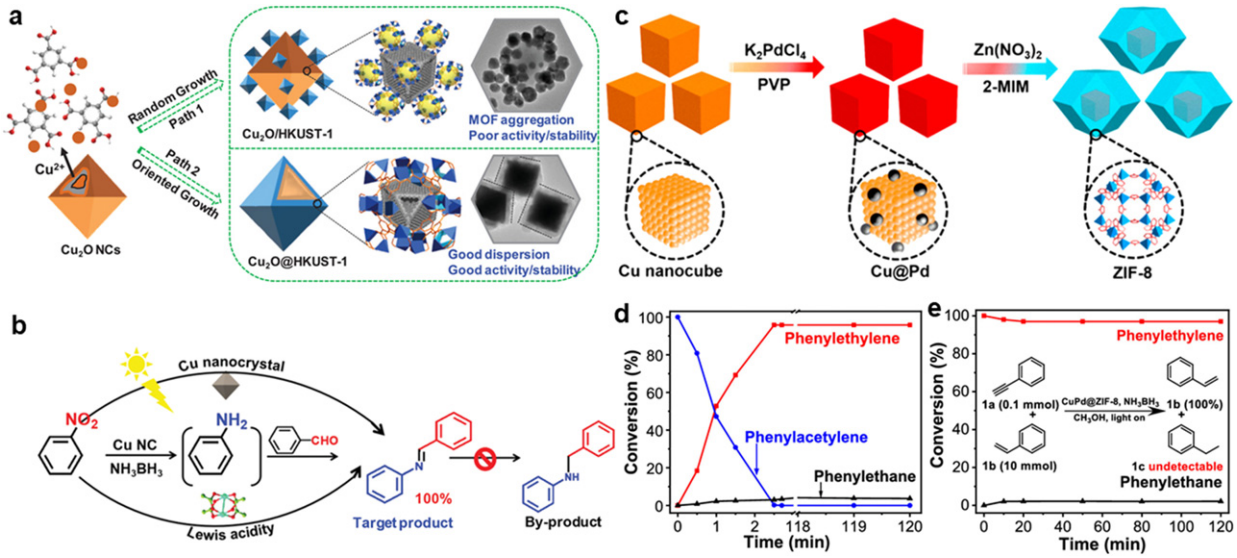

Fig. 4 (a,b) General illustration of synthetic method for Cu_2O@HKUT-1 and catalytic performance for nitrobenzene hydrogenation and reductive amination of benzaldehyde, (c) synthetic scheme of CuPd@ZIF-8 and (d,e) CuPd@ZIF-8 catalyzed time dependent hydrogenation of phenyactylene (d) and phenyethylene (e) by using ammonia borane as hydrogen source under light-irradiation. Reproduced from (a,b) Wang, L., *et al.*, 2021. Encapsulating copper nanocrystals into metal-organic frameworks for cascade reactions by photothermal catalysis. Small 17, e2004481. (c-e) Li, L., *et al.*, 2020a. Accelerating chemo- and regioselective hydrogenation of alkynes over bimetallic nanoparticles in a metal–organic framework. ACS Catalysis 10 (14), 7753–7762.

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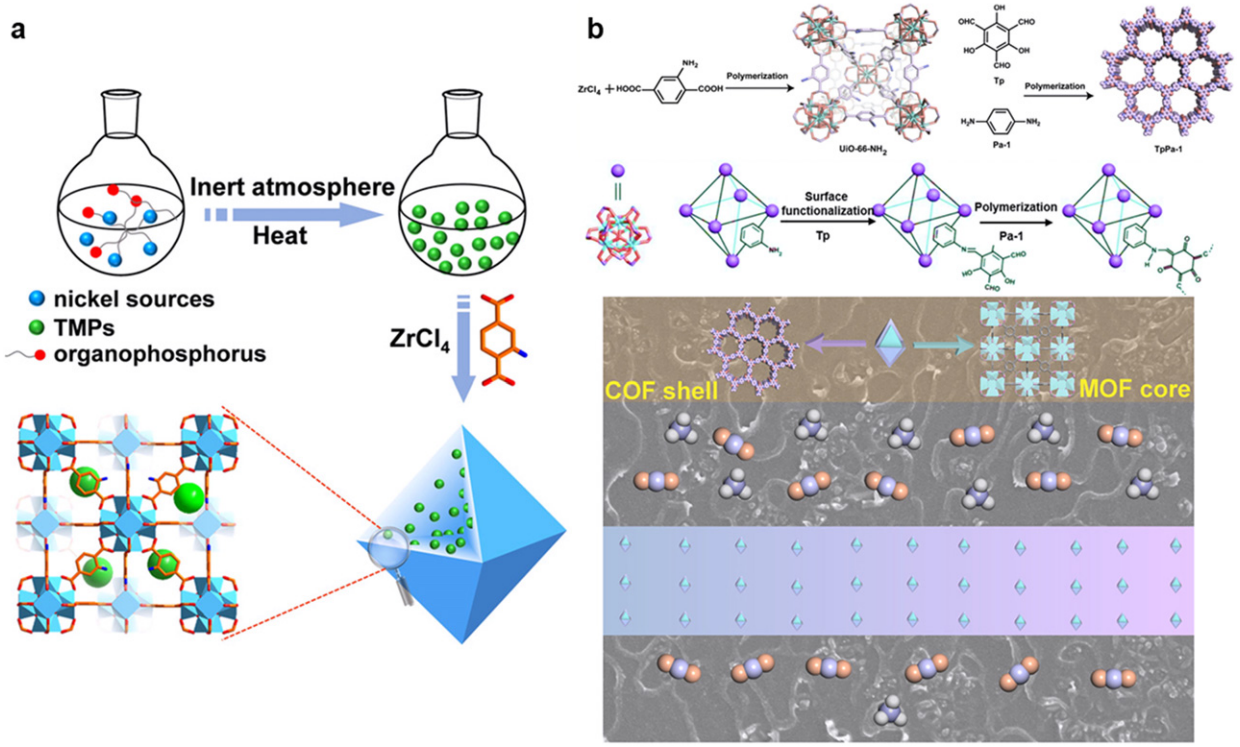

Fig. 5 (a) Schematic illustration of transition metal phosphides and their MOF-based composites (b) schematic illustration of MOF@COF mixed matric membrane for CO_2 permeability and CO_2/CH_4 selectivity. Reproduced from (a) Sun, K., *et al.*, 2020. Incorporating transition-metal phosphides into metal-organic frameworks for enhanced photocatalysis. Angewandte Chemie 59 (50), 22749–22755. (b) Cheng, Y., *et al.*, 2019. Mixed matrix membranes containing MOF@COF hybrid fillers for efficient CO_2/CH_4 separation. Journal of Membrane Science 573, 97–106.

interfacial interactions between the MOF and metal ions, which subsequently converted into surficial-grown metal-sulfide nanoparticles. These MOF-nanoparticle composites showed better charge separation/transfer ability and resulted in the enhanced photocatalytic performance. For instance, the MIL-101@CdS composites are proved for the photo-reduction of Nitro-functional group in aromatic compounds and attributed the charge transportation and separation capability of this composite (Lin *et al.*, 2020). It should be noted that the use of CPM as a catalyst has greater advantages, such as high catalytic efficiency, short diffusion distance, catalyst regeneration is easier. Recently our group has assembled the pre-synthesized tiny monodisperse Ni_2P_5 into Zr-MOF (Zr_6 $O_4(OH)_4$ $(BDC\text{-}NH_2)_6NH_2$ = 2-amino-1,4-benzenedicarboxylic acid), to give the corresponding composite (**Fig. 5**(a)) (Sun *et al.*, 2020). Which meaningfully boosted the photocatalytic H_2 production performance and Ni_2P_5 NPs exhibit production rate than Pt NPs.

Gas adsorption and separation

CPMs have received great attention in the field of gas adsorption and storage due to their extremely high surface area, pore capacity and porosity ratio It has been reported that the crystal structure and size of CPM affect their adsorption behavior, including the adsorption amount and adsorption dynamics (Jiang *et al.*, 2010a; Lan *et al.*, 2011). The smaller the particle, the larger the surface energy, the shorter the diffusion distance, the absorption volume may become larger; In addition, the size of the particles can also affect the adsorption behavior of flexible COFs and MOFs (Wu *et al.*, 2021).

Cheng *et al.* (2019) reported a mixed matrix membrane by incorporating UiO-66-NH_2@TpPa-1 into commercial polysulfone (PSf) with the addition of 5 wt% UiO-66-NH_2 @TpPa-1. UiO-66-NH_2@TpPa-1 (MOF@COF) mixed matrix membrane exhibited significant improvement in CO_2 permeability and CO_2/CH_4 selectivity due to the factors that UiO-66-NH_2 with appropriate pore size (5. 1 Å) has high CO_2 adsorption affinity and excellent chemical stability, while COF TpPa-1 with excellent stability and large pore size (18.3 Å) can prevent the pore blockage of UiO-66-NH_2 and quickly establish channels for gas permeability (**Fig. 5**(b)).

Biomedicine

Compared with known lipids, polymers, metal clusters, carbon materials, oxides, metal nitrides and other drug carriers, MOFs as a drug carrier have many advantages, such as can overcome many drug instability, poor water solubility, toxicity and other shortcomings, but also to achieve high load and drug slow release (Feng *et al.*, 2012). Adjustable pore structures, diverse

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Synthetic Methods	Advantages	Disadvantages
Solvothermal	Using solvothermal method, some MOFs and COFs can be synthesized on a large scale	High temperature,. Solubility dependent, time-consuming
Ionothermal	Simple, mild, and green method	High Temperature, time-consuming. The most applied monomers in an ionothermal method are amorphous materials and lack long-range molecular orderings
Microwave	Lower reaction time and also forms the cleaner products. Synthesis progress can be visualized, and the reaction temperature and pressure can be controlled simultaneously	It needs to control the synthesis conditions. It needs temperature and in some cases high temperature
Sonochemical	Fast and cost-effectiveness. This method considers as green method	Controlled the synthesis conditions and temperature and in some cases high temperature are required.
Mechanochemical	Simple, fast, solvent-free, room temperature, economical and environment friendly	In this method, we can only use some building monomers
Light promoted	Simple and cost-effective, sunlight irradiations are required	Limited to light sensitive building monomers
Room temperature	This method is simple, easy, cheap, and also green	we can only use some building monomers

Fig. 6 Comparative presentation of advantages and disadvantages of different synthetic methods for crystalline porous materials (CPM).

compositions, and the internal environment enable MOFs to load large quantities of drugs with different physical and chemical properties, which can be loaded not only on the pores or surfaces of MOFs, but also as part of the MOFs skeleton to form so-called bio-MOFs. In addition, controlling the particle size of MOFs plays a critical role in drug delivery and bio imaging applications (Jiao *et al.*, 2019). Micron MOFs can be used to have higher permeability and EPR effect, and play a better role in the integration of diagnosis and treatment of malignant tumors (Giménez-Marqués *et al.*, 2016). The use of iron (III) base MOFs as a non-toxic drug carrier that can be loaded with hydrophilic, hydrophobic, and kinky drugs, which is difficult to do with conventional materials (Horcajada *et al.*, 2010; Chalati *et al.*, 2011b). MOFs also have good application prospects in bio imaging (Shah *et al.*, 2018).

Conclusion and prospective

In recent years, MOFs and COFs materials with large aperture and high ratio surface area has become one of the hot research topics of crystalline porous material (CPM). The preparation methods are simple, the reproducing methods are diverse, and the vast majority of materials can maintain the integrity of the skeleton after removing solvent molecules from the pores. Compared with some large monocrystalline materials, the synthesis and application of micro-nanomaterials have attracted people's attention in recent years. Because of its small size and its super-high surface area, orderly pore structure and other advantages, it has potential application prospects in catalysis, gas storage, sensing, proton conductors, biomedicine and so on.

This article briefly introduces the synthesis methods of micro-nano MOFs/COFs materials including solvothermal method, microwave heating method, co-precipitation method, mechanochemical, and micro-emulsion method. Experimental conditions such as reaction temperature and time, pH, molar ratio of metals and compounds, types of surfactants and regulators, and dosage can be changed to effectively regulate the appearance and size of COFs and MOFs. It should be explained that different preparation methods are more or less there are shortcomings and shortcomings, such as the method is not universal, product preparation cycle is long, product shape size uniformity is poor, so find a common can be prepared out of uniform size, shape control, with complex structure and appearance of COFs/MOFs preparation method is still extremely challenging. In the preparation of MOFs, the size and appearance of the product can be regulated by introducing acidic or alkaline regulators, which play different roles in controlling the shape and size of MOFs: Alkaline regulators accelerate the nucleation process by producing many small crystals quickly through the effect of decontamination, and then obtain relatively small-sized products, while acidic regulators inhibit the nucleation process by competing with ligands to obtain relatively large products. At the same time, by introducing surfactants, MOFs with a single dispersion and a more even size can be obtained. It should be emphasized that the self-assembly of MOFs materials in 3D space is much more complex than 2D materials, and there is little reporting on the preparation of 3D materials using hard template methods, soft template methods, and liquid-liquid, gas-liquid interface reactions.

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The variety of synthetic methods for obtaining COFs/MOFs are as diverse as the chemistry of the MOFs/COFs themselves. Although all methods have their strengths and complement each other, it is useful to equate the influence on the structural properties of obtained materials. It is also important to understand scalability, yield and efficiency. The methods, discussed herein, have advantages and disadvantages, which are presented in **Fig. 6** for general comparison.

Although scientists have made some achievements in the field of MOFs/COFs, but based on the above introduction and analysis, we find that, in addition to the preparation methods described above, there are shortcomings, most of the research results are limited to a very small number of MOFs, such as IRMOFs, ZIF-8, HKUST, UiO-66, MIL series, and most of the products have poor shape uniformity, its growth engine is rarely discussed. The synthesis of COFs and MOFs with complex shapes and structures, such as nuclear-shell structures, hollow structures etc., are rarely reported. In addition, the study of these self-assembly process should aim at their eventual ability to assemble into devices, but this research is still in its infancy. Therefore, scientists still face great challenges in the synthesis, shape regulation, mechanism discussion and application of CPMs. At the same time, we firmly believe that the synthesis methods of CPM should be further developed, including the control of MOFs/COFs composites, size, shape and corresponding theoretical research, and ultimately the application of such materials in catalytic, separation, adsorption, biomedicine and sensing related fields.

Acknowledgment

This work is supported by the NSFC (2021YFA150040, 22161142001, 21725101, 21871244) and International Partnership Program of CAS (211134KYSB20190109).

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