Towards industrializing metal-organic frameworks : scalable synthetic means and their transformation into functional textile materials

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**TOWARDS INDUSTRIALIZING METAL-ORGANIC
FRAMEWORKS: SCALABLE SYNTHETIC MEANS AND
THEIR TRANSFORMATION INTO FUNCTIONAL TEXTILE
MATERIALS**

TEO WEI LIANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

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FRAMEWORKS: SCALABLE SYNTHETIC MEANS AND
THEIR TRANSFORMATION INTO FUNCTIONAL TEXTILE
MATERIALS**

TEO WEI LIANG

SCHOOL OF PHYSICAL AND MATHEMATICAL SCIENCES

A thesis submitted to the Nanyang Technological
University in partial fulfilment of the requirement for the
degree of Doctor of Philosophy

2021

Statement of Originality

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Yanli Zhao

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Zhao Yanli

Authorship Attribution Statement

This thesis contains material from 4 papers published in the following peer-reviewed journals / from papers accepted at conferences in which I am listed as an author.

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The contributions of the co-authors are as follows:

- Professor Yanli Zhao and I provided the structure for this review paper.
- I prepared the manuscript drafts.
- Professor Yanli Zhao, Dr Weiqiang Zhou and Dr Cheng Qian reviewed the manuscript draft.

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- Professor Yanli Zhao and I came up with the research idea.
- I designed the experimental details.
- Siti Khadijah Binte Ariff and I performed the experiments, including synthesis and most of the characterizations (PXRD, N₂ adsorption/desorption study, SEM, ATR-IR and TGA) for the materials.
- Dr Deblin Jana performed the XPS characterization.
- I analyzed the data and prepared the manuscript drafts.
- Professor Yanli Zhao, Dr Weiqiang Zhou and Dr Soo Zeng Fiona Phua reviewed the manuscript draft.

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The contributions of the co-authors are as follows:

- Professor Yanli Zhao and I came up with the research idea.
- I designed the experimental details.
- I synthesized and characterized all materials prepared.
- Dr Jiawei Liu conducted computational simulations and calculations.
- Dr Jiawei Liu and I carried out bacterial studies on the prepared materials.
- I analyzed the data and prepared the manuscript drafts.
- Professor Yanli Zhao, Dr Weiqiang Zhou and Dr Jiawei Liu reviewed the manuscript draft.

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The contributions of the co-authors are as follows:

- Professor Yanli Zhao and I came up with the research idea.
- I designed the experimental details.
- I synthesized and characterized all materials prepared.
- I conducted dye absorption studies on the prepared materials.
- Dr Jiawei Liu conducted computational simulations and calculations.
- Dr Jiawei Liu and I carried out bacterial studies on the prepared materials.
- I analyzed the data and prepared the manuscript drafts.
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Teo Wei Liang

Abstract

For over two decades, metal–organic frameworks (MOFs) have drawn significant attention in the scientific community. Compared to other porous material types, MOFs possess unique properties due to the presence of both metallic and organic components embedded within the framework structure. This gives rise to a multitude of structural variations via permutation and combination. Furthermore, post-synthetic methods for material modification allow for greater customizability to suit the intended purpose, with the hope to solve a wide variety of real-world problems. Indeed, the development of MOF for various practical applications has created fascinating new areas of research and pushed the boundary of scientific advancement.

Despite overwhelming interests for this unique class of porous materials, the progress towards actual utilization falls short of the expectation due to the challenging transition from academia to industry. Despite their importance to the commercialization of MOFs, large-scale production and processing of MOFs materials are not well explored. For MOFs to realize their full potential as a solution to real-world problems, it is critical to develop effective strategies which are cost effective and feasible to be adapted for industrial use. In this thesis, I will explore efficient MOF synthetic methodologies and processing techniques, with the aim towards the eventual goal of MOF commercialization.

In chapter 1, a broad overview of MOFs will be introduced. An extensive literature review exploring the current state of MOF research will be presented. Specifically, progress on large-scale MOF synthesis and their subsequent processing into functional materials will be discussed in detail. At the end of the chapter, opportunities for MOF research towards industrialization and commercialization will be highlighted and the thesis objective will be defined.

After which, in chapter 2, a facile synthetic methodology which eliminates the use of HF and solvent to produce flexible chromium-based MOFs will be discussed. Using this methodology, 2 different isomorphous flexible MOFs can be obtained selectively, depending on the type of metallic salt used. This improved green synthetic procedure could be adapted for the large-scale preparation of these flexible MOFs in the future.

Then, in chapter 3, a facile and efficient strategy to embed MOF powder onto fabric substrates using a poly(acrylic acid) binder will be introduced. This process minimizes waste production and can be applied to different types of MOFs and fabric substrates. The prepared MOF-fabric composites can be used for the industrial production of functional protective wearables against microbial activities.

Following that, in chapter 4, the development of a gram-scale synthesis for archetypical ZIF-8 MOF and its subsequent processing into fabric substrate will be described. This procedure allows for low temperature, instantaneous production of ZIF-8 in high yield. The prepared ZIF-8 was also easily coated onto fabric substrates using poly(styrene) as a binder. The resultant composite was shown to be effective in dye adsorption and possess anti-bacterial properties.

Lastly, in chapter 5, a summary concluding the various projects, which constitute this thesis, will be presented. A brief outlook of the future for MOF industrialization will also be discussed.

Through various methods of producing and processing MOF material discussed in this dissertation, I hope to bridge the gap between scientific research and industrial needs, to truly develop MOFs into useful and functional materials for the future.

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Chapter 1

Introduction

1.1 Metal Organic Framework

1.1.1 Introduction

Figure 1. Construction of Metal-Organic-Framework (MOF) from inorganic metal and organic linker SBUs.

Metal-Organic Frameworks (MOFs), sometimes referred to as coordination polymers, are made up of inorganic metal and organic linker secondary building units (SBUs), held together by coordination bonding to form an infinite array of repeats (Fig. 1).¹⁻³ This class of porous crystalline material, often with aesthetically pleasing molecular structures, has captured the interest of material scientists for the past two decades. With larger porosity and surface area compared to traditional zeolites,⁴ MOFs have the potential to outdo or even replace existing porous materials in years to come. Industries have also noticed the potential of MOFs, as evident from the recent attempts to commercialize MOF-based products. Industrial giant, BASF, took the lead in 2013, pledging to support the production of MOFs for gas storage purposes.⁵ We have also seen start-ups, such as NuMat technologies, emerging to seize new business opportunities to commercialize MOFs.⁶

Figure 2. Several archetypal MOFs: MOF-5, HKUST-1, MIL-101, ZIF-8, UiO-66 and MOF-74.

Multitopic linkers based on carboxylate and N-heterocyclic functional groups, such as benzene-1,4-dicarboxylic acid (BDC), benzene-1,3,5-tricarboxylic acid (BTC) and 2-methylimidazole (mim), were extensively studied during the initial stage of MOF research, which gave rise to several archetypal MOFs. One of the earliest MOF reported was MOF-5, comprising of BDC and Zn_4O SBUs to give an open cubic framework structure, with an astonishing large Langmuir surface area of $2900 \text{ m}^2\text{g}^{-1}$.⁷ At around the same period of time, HKUST-1 was reported, using BTC and Cu paddlewheel as SBUs.⁸ Other prominent MOFs, such as MIL-101,⁹ ZIF-8,¹⁰ MOF-74¹¹ and UiO-66¹² soon followed as the research field develops. These archetypal MOFs (Fig. 2) remain important today as their readily available precursors and relative stability in air allow for potential practical uses. They also lay the

foundation for our understanding of MOFs, to design and construct more elaborated species as the field progresses.

The success of MOFs has also inspired the development of many other related field of research, including Metal-Organic Polyhedrals (MOPs),¹³⁻¹⁴ Covalent Organic Frameworks (COFs)¹⁵ and Hydrogen-bonded Organic Frameworks (HOFs).¹⁶ Together, these new classes of porous framework materials have the potential to address many of the world's problems in years to come.

1.1.2 Framework Design and Considerations

Figure 3. Length and functionality modification for organic linker SBUs in MOFs.

The 2 components that made up MOFs, namely the inorganic metal and organic linker SBUs, are essential for the construction of the framework structure. In particular, the organic portion received plenty of attention, as knowledge from the well-established field of organic synthesis can be effectively utilized for the design and creation of linkers used in MOF construction. By changing the length and functionalities present on the organic linker (Fig. 3), properties of the resultant framework, such as the pore aperture, void space, pore chemistry

etc., can be modified to achieve the desired outcome. For example, our group had designed and synthesized linkers using “azide-alkyne click chemistry” to introduce nitrogen atoms, which significantly improves CO₂ capture and conversion.¹⁷⁻¹⁸ Also, different combinations of organic linkers and inorganic metal SBUs further increase the theoretical number of MOF structures that could be produced, making MOFs highly tailorable and customizable for their intended purposes.

1.1.3 Postsynthetic Modification

Figure 4. Postsynthetic modification (PSM) of organic linkers within MOFs via imine and amide condensation reactions.

Also, the versatility of MOF materials can be further enhanced by subjecting MOFs to post-synthetic modifications.¹⁹ Some reactive functional groups cannot be incorporated directly into MOF via linker design, as they will interfere with the framework construction during MOF formation. By making use of the organic functionalities on linkers of MOFs, further chemical transformation can be carried out on the backbone of the framework structure. Majority of the chemical transformations rely on amine or aldehyde moieties present on the framework backbone, via amide and imine condensation reactions respectively, to attach a pendant group onto the MOF structure (Fig. 4). In one of the earliest study, Lin and coworkers have successfully introduced optical contrasting agent (BODIPY dye) and anti-cancer cisplatin prodrug into Fe-based MIL-101 nanoparticles.²⁰ Acylation via condensation reaction covalently grafted the pendant groups onto the -NH₂ groups present on the MOF backbone

postsynthetically. The attached groups can then be released when tested in vitro with HT-29 cell line, giving one of the earliest MOF-based drug delivery system. In another study, Caro et. al. have successfully immobilized ZIF-90 MOF particles onto an Al_2O_3 support to form a functional membrane.²¹ This was a result of condensation reaction between aldehyde groups present on ZIF-90 nanoparticles and amine-functionalized Al_2O_3 surface. The resultant membrane shown excellent gas separation property for H_2 due to molecular sieving effect of ZIF-90 MOF present. As such, postsynthetic modification allows for further modification of MOFs to create new functional materials.

1.1.4 Applications of MOFs

Figure 5. Several important practical applications for MOFs, such as gas capture, separation, sensing and catalysis.

Given the versatility of MOFs, it is not surprising that MOFs has been regarded as an emerging new material for a vast variety of applications (Fig. 5).²² Over the years, numerous studies explored unique ways to utilize MOFs to solve a vast range of real-world problems. Several important fields of study for MOF application include gas storage,²³⁻²⁵ separation,²⁶ sensing²⁷⁻²⁸ and catalysis²⁹ etc. Other new areas of research such as biomedical³⁰⁻³¹ and water harvesting³² among others, are growing as well.

One of the earliest applications for MOF-based materials is gas storage. Their large surface area and periodically ordered structures make them ideal for the capture of gases, such as H₂,²³ CO₂,²⁴ and CH₄.²⁵ As global consumption for energy increase, H₂ is envisioned to be a clean alternative fuel source as only water is formed from its combustion. One of the earliest MOF reported, MOF-5, was shown to exhibit superior H₂ storage capability,³³ which aroused the interest of many scientists and engineers worldwide. Similarly, natural gas storage was also an attractive viable option as an alternative fuel. Due to the non-polar nature of both gases, physisorption was heavily relied upon for the capture and storage of these gases. CO₂, on the other hand, can be absorbed via chemisorption by MOFs with open metal sites or basic functional groups. An important consideration would be the practical conditions in which such operations are typically carried out. High pressure, drastic temperature changes and impurities in gases would significantly decrease the efficiency of such processes. The combination of both experimental and theoretical calculations is necessary to understand and improve the design of MOF-based gas storage systems.

Separation of chemical species using MOFs is another important practical application.^{26, 34-35} MOFs are very suitable for the separation of closely related molecules, as it is easy to modify their structure. One of the earliest use of MOFs in chemical separation was for the treatment of flue gas mixture. Based on similar principle used in CO₂ storage, MOFs can be designed with enhanced selectivity for CO₂ over the other flue gas components, namely,

N₂ and H₂O. Molecular sieving effect can also give rise to selectivity by controlling the pore aperture of MOF used. This is especially useful for the separation of industrially useful gases mixtures such as C₂H₄/C₂H₂, Xe/Ke, D₂/H₂ and several other alkene/alkane mixtures. Also, liquid phase separation with MOFs is possible as well. Organic molecules, such as phenolic compounds, explosives, pharmaceuticals, and dyes, are routinely discharged into water sources and produce undesirable effects for the environment and public health. Till date, numerous studies have demonstrated the potential of MOF as an effective material for the separation of these species in water treatment.

Detection and sensing of chemical species are essential for analytical chemistry. By utilizing the interactions between analytes and framework backbone, MOFs can serve as effective luminescence chemical sensors.^{27, 36-37} Aromatic or π -conjugated organic linkers can introduce luminescence property to the resultant MOF generated. Most ligands are able to interact with lanthanides via antenna effects to give luminescence for lanthanide-based MOFs. Furthermore, MOFs can serve as host to luminescent guests, such as quantum dots, organic dye molecules and metal complexes. Luminescent MOFs are able to detect a wide range of species, from explosive nitroaromatics to heavy metal ions. Furthermore, luminescence emission can be fine-tuned to give different responses to different species present, allowing for the detection of multiple analytes. Emission color can also be tuned by adjusting the types and ratio of Ln³⁺ ions. In particular, colorimetric emission can potentially be developed into real-time sensing materials for non-quantitative detection of chemical species.

MOFs are also useful as heterogenous catalysts.^{29, 38} The periodic arrangement of MOFs allows for even distribution of catalytically active metal center within the framework structure. Porous channels within the framework further facilitate the transport of materials in and out of the MOFs. Their robustness and insolubility in a wide variety of solvents are ideal for recycling of catalyst without significant leaching. Till date, MOFs have been used for numerous catalytic

transformations, including CO₂ conversion, H₂ evolution, selective oxidation of alkenes and alcohols, reduction, cross-coupling reactions, among others. These catalytic systems are very efficient, with many achieving good yield and selectivity. Recently, MOFs have been used as precursors to produce single-atom catalysts.³⁹ Taking advantage of the unique structure of MOFs, well distributed catalytic sites consist of metal atoms can be obtained, which holds promising potential as effective catalysts in chemical transformations.

1.2 Commercialization of MOFs

Apart from the promising research outlook in the scientific community, the commercialization of MOFs for industrial uses is also a very prominent area of development. One of the earliest attempts was the use of MOFs for natural gas storage, an initiative by BASF.⁵ Start-ups, including NuMat Technologies, were also established from academia's success, providing storage solutions such as Ion-X.^{6, 40} Numerous companies also joined effort to promote MOF products, such as UK-based MOF Technologies and Switzerland-based NovoMOF. Despite these encouraging efforts, the development of MOFs for real-world application is still at its infancy. The lack of synthetic methods to prepare MOFs in large quantity greatly impeded the progress of MOF industrialization. Most academic studies in the laboratory produce MOFs at the milligram scale, which significantly differ from industrial requirements. Scalability and cost-effective production means were not widely investigated and are often limited to primitive MOF types.⁴¹ In addition, most MOF-based materials produced are in the powder form, which also restrict their uses in practical situations. Powdered materials are harder to handle, often requiring costly and time-consuming techniques, such as centrifugation.⁴²⁻⁴³ They also pose inherent safety issues when utilized, such as respiratory health risks. Downstream processing of MOF powders into usable products is very limited, as there is lesser motivation to develop commercially viable products in the academic scene as

compared to industrial players. As such, this situation results in a huge gap for the realization of MOFs as a practical solution to many real-world problems.

1.2.1 Scalable Synthesis of MOFs

Developing synthetic methodologies for the industrialization of MOFs is an important challenging step in the commercialization process. Typically, industrial requirements differ significantly from that of laboratory, with scalability, cost efficiency and quality control as key parameters to evaluate the effectiveness of an industrial synthetic procedure. Most research on MOFs in academia did not focus on the production of MOF materials themselves, which cannot be overlooked from a commercial perspective for the industrialization of MOFs. This represents the biggest gap between academia and industrial research in translating MOF technology for real-world use.

1.2.1.1 Base-assisted Synthesis

By far, the most widely used method to obtain MOFs is via the conventional solvothermal approach. Metal salts and organic linkers were incubated at a preset temperature for a duration of time during MOF crystallization. This process was especially well developed for the milligram scale synthesis of MOF powders, which is the typical synthetic method of choice in most research articles. However, it is difficult to translate this method to larger scale synthesis. The lack of scalable means for this methodology imposed a major hurdle toward its adaptation for industrial use. Apart from the scalability problem, several drawbacks also suggest that such a method is inappropriate for the cost-efficient industrial production of MOFs. The process usually involves excessive use of organic solvents during the synthesis and washing steps. Crystallization for MOFs is slow and often requires heating, increasing both

energy and time costs during the production. In order for this method to be relevant for the bulk production of MOFs, improvements must be made to increase its efficiency.

One successful example is through the use of base to induce rapid crystallization of MOFs in an aqueous environment. By using deprotonated carboxylate linkers or metal hydroxides as precursors, rapid crystallization of MOFs can be achieved. In addition, this technique uses greener solvents (e.g., water and ethanol), as deprotonated linker salts become more soluble in protic solution. This process would remove the inherent safety and cost concerns associated with organic solvents typically used in batch reactions. The reaction time varies from an instant to a day, and heating may not be necessary. With reduced reaction time for MOF products to form, it seems more plausible for this synthetic methodology to be adopted for bulk synthesis. Several studies (Fig. 6) showed that this method is applicable for the synthesis of various MOFs, such as HKUST-1,⁴⁴⁻⁴⁵ MIL-100(Fe),⁴⁶ MOF-74,⁴⁷⁻⁴⁸ MOF-5,⁴⁸ and MIL-53(Al).⁴⁸

Figure 6. (a) SEM image of HKUST-1 synthesized using Cu(OH)₂ in 5 min. (b) N₂ adsorption/desorption curves for MIL-53(Al) synthesized at room temperature as compared to the same material synthesized using conventional solvothermal method at 220°C. (c) Schematic illustration describing the facile synthesis of MIL-100(Fe) using NaOH. Reproduced with permission from ref 45, 46 and 48.

One of the earliest reports by Pérez-Ramírez and coworkers utilized this strategy to synthesize HKUST-1 from $\text{Cu}(\text{OH})_2$ and trimesic acid.⁴⁵ Facile mixing of the two reagents gave quality HKUST-1 crystals (Fig. 6a), comparable to commercially available HKUST-1 and Basolite C300. This process uses a greener solvent (i.e., ethanol), compared to dimethylformamide (DMF), and requires no heating, which are great advantages when compared to existing solvothermal method. Furthermore, quantitative yield was obtained. The process was also shown to be scalable using a 5L mini pilot reactor to produce 284 g of HKUST-1 in a single batch. This work inspired the search for similar base-assisted methodology for other MOF types. Díaz et al. adopted a similar strategy by deprotonating terephthalic acid, a common organic linker used in MOF synthesis, with basic NaOH.⁴⁸ They explored the generality of this strategy by applying it to the synthesis of terephthalic acid based MOF-5 and MIL-53(Al), as well as 2,5-dihydroxyterephthalic acid-based MOF-74. Water was used as the solvent and the synthesis was carried out at room temperature for 20–24 h. The products isolated have similar intrinsic porosity as those derived from solvothermal method (Fig. 6b). Sanchez-Sanchez and coworkers utilized the same strategy with trimesic acid and Fe salt to obtain MIL-100(Fe) (Fig. 6c).⁴⁶ Similarly, water was utilized as the solvent and the reaction was carried out at room temperature. The synthesis was carried out at gram scale for 24 h, with a high yield of 76%. Characterization of the prepared MIL-100(Fe) showed that it is similar to its solvothermal counterpart. More importantly, this method avoided the use of corrosive HF as an additive during the synthesis, greatly improving the feasibility of preparing MIL-100(Fe) on a large-scale. By addressing some of the shortfalls for conventional solvothermal synthesis, base-assisted synthesis offers a unique solution with a promising potential for the large-scale batch synthesis of MOF powders.

1.2.1.2 Microwave Synthesis

Microwave heating utilizes interactions between the electromagnetic field generated and the dipole moments of molecules for more effective energy transfer from the source to the target.⁴⁹ It is typically faster and penetrates deeper into reaction mixture compared to conventional heating, making it an attractive option for the synthesis of MOF products. One of the earliest attempts using microwave for MOF synthesis was reported by Chang and coworkers.⁵⁰ MIL-101(Cr) was synthesized at 210°C with microwave irradiation. Quality crystalline MOF was formed over 40 min, a huge decrease in time taken compared to conventional heating (10 h) under similar conditions. The resultant crystals were also found to be smaller, due to the rapid crystallization induced by microwave heating. There were negligible differences in the quality of MIL-101(Cr) crystals synthesized by microwave compared to conventional heating, as analyzed by various characterization methods. This study shows that microwave synthesis is a viable alternative for the production of MOF products. Similar results were reported for other MOF types, such as MOF-5,⁵¹ ZIF-8,⁵² MOF-74,⁵³ and UiO-66.⁵⁴ While it looks attractive as a potential option, microwave synthesis was not widely explored for the bulk production of MOFs. Penetration depth of microwave is the major limitation for scaled-up operation using microwave, which results in the uneven heating of contents within a large reaction chamber. However, this could be addressed by combining microwave synthesis with other methods.

1.2.1.3 Flow Chemistry

Figure 7. (a) Schematic illustration describing the synthesis of HKUST-1, UiO-66 and NOTT-400 using continuous flow production. (b) Slurry of MIL-53(Al) produced using flow chemistry. Commercially available MIL-53(Al) (left) compared with as-synthesized sample (right). A 50 pence piece was included to illustrate the scale. (c) PXRD pattern of ZIF-8 synthesized using flow chemistry as compared to the simulated pattern. Reproduced with permission from ref 56, 57 and 58.

One alternative to solvothermal synthesis is to use a flow chemistry set-up.⁵⁵ As compared to batch production, a major advantage of using flow chemistry is its continuous production, which facilitates industrial manufacturing. Pump actions direct the flow of chemicals through internal tubing, with the continuous input of reagents on one end, and continuous output of products on the other. In addition, flow chemistry generally reduces the time and energy taken during the synthesis, due to more effective mixing of reactants and efficient energy transfer. Compared to batch reaction, continuous flow reactions do not suffer from the inherent problem of scaling, such as safety concerns when handling large quantity of chemicals and down time between batches. All of these factors make the process more cost efficient and streamlined. As such, there are several notable studies using flow chemistry to

produce MOFs in large quantities. In 2014, Hill and coworkers reported one of the earliest uses of flow chemistry to give HKUST-1, UiO-66 and NOTT-400 MOF products (Fig. 7a).⁵⁶ The product quality was verified by characterization tools to ensure the purity. This study proves that it is feasible for MOFs to be produced using flow chemistry, laying the foundation for future work. At around the same time, Schröder and coworkers did a study to compare between batch production and flow production for the synthesis of MIL-53(Al).⁵⁷ Flow technique was shown to be superior, producing more than 500 g of MIL-53(Al) slurry in a 4 h time frame (Fig. 7b). In addition, they showed that their set-up can be readily adapted to other MOF types, such as HKUST-1. These studies demonstrated the practicality and feasibility of flow chemistry for the industrial production of different MOFs.

Flow chemistry can also be combined with other strategies to achieve synergistic enhancement in the production process. By incorporating base-assisted strategy, Lester and coworkers utilized a flow set-up to obtain ZIF-8 nanocrystals (Fig. 7c).⁵⁸ They were able to eliminate the use of heat for MOF crystallization in the synthesis. The use of alternative source of heating with flow chemistry set-up was also widely investigated. Ranocchiari and coworkers studied the effect of using microwave irradiation to replace conventional heating for MOF synthesis using flow chemistry.⁵⁹ Because of the thin tubing in flow chemistry, microwave irradiation can penetrate more effectively to achieve the desirable heating effect. As such, the use of flow set-up successfully circumvented the limitation pose by microwave penetration, allowing for its use in large-scale production of MOFs. The team was able to successfully utilize microwave irradiation strategy to yield UiO-66, MIL-53(Al) and HKUST-1 in multi-gram scale. Similarly, ultrasound was utilized by Jhung and coworkers for the synthesis of MIL-53(Fe).⁶⁰ The modified flow set-up was compared with similar experimental ran using microwave irradiation and conventional heating. A detailed analysis on the nucleation and growth of MOF crystals suggested that both ultrasound and microwave significantly

accelerated the crystallization process. By using more efficient method for heating, the energy cost can be further reduced, making flow chemistry a more attractive option for large-scale production of MOFs. Despite the significant advantage of using flow chemistry as compared to batch production, one must keep in mind the inherent drawbacks when using the flow set-up. A typical problem associated with using flow chemistry for MOF synthesis is the possibility of clogging. MOF nanocrystals synthesized are in the solid phase, which can impede the flow within the narrow tubing used, building up backflow pressure in the system. Nevertheless, this strategy provides an alternative pathway to the batch production and remains as an important process to be considered for the industrial production of MOFs in the future.

1.2.1.4 Electrochemistry

The use of electrochemistry for MOF synthesis is one of the earliest methods explored for the effective bulk production of MOFs. By using electrical current to induce redox reactions, organic linkers and metal ions can form coordination bonds rapidly to give MOF products. Electrochemical reaction conditions are usually milder, and the process is much faster

Figure 8. (a) Actual electrolytic cell used for the production of HKUST-1. (b) Schematic diagram for the electrolytic synthesis of UiO-66-NH₂. Reproduced with permission from ref 61 and 68.

compared to conventional solvothermal routes. In 2006, BASF introduced the electrochemical synthesis of HKUST-1 (Fig. 8a).⁶¹ The use of metal electrodes further eliminated the need for metal salt precursors, reducing the effect of anion corrosion. This study lays the groundwork for future investigation of MOF production using electrochemistry. Subsequent research was focused on controlling the shape and size of MOF particles formed. Generally, changes in electrical current and solvent composition affect the morphology of the resultant MOFs significantly.⁶²⁻⁶⁴ Electrochemical method was also applied to other MOF types, such as MOF-5,⁶⁵ ZIF-8,⁶⁶ MIL-100(Al),⁶⁶ MIL-53(Al),⁶⁶ MIL-53-NH₂(Al),⁶⁶ MIL-100(Fe),⁶⁷ and UiO-66-NH₂ (Fig. 8b),⁶⁸ which proved that this is a versatile and effective method for the production of MOFs in general. Most of these studies are targeted at exploring various possibilities of MOF production via electrochemical means, establishing electrochemical method as a useful method for MOF synthesis. However, most reports listed above are merely laboratory scale set-up, so it is not easy to gauge their potential upon scaling up.

Despite many advantages of producing MOF electrochemically, this methodology has its own set of challenges that needs to be address. MOF production using electrochemistry is often limited by the amount of electrochemically active sites available for redox reactions to occur, which diminishes as MOFs begin to form on the surface of electrodes. Also, the synthesized crystalline products are usually attached to the electrodes. Therefore, an additional step of dislodging the porous crystals from the electrode supports is necessary to obtain the powdered products when adhesion to electrode surfaces occurs. But compared to conventional solvothermal method, this method represents an improvement in the production of MOFs.

1.2.1.5 Supercritical CO₂

Figure 9. (a) Experimental set-up for the synthesis of ZIF-8 using ScCO₂. (b) ZIF-8 produced by ScCO₂ synthesis. A 25 cent Canadian coin was included to illustrate the scale. (c) Schematic illustration for the synthesis of UiO-66 using ScCO₂. Reproduced with permission from ref 73 and 74.

Another popular strategy of choice is the utilization of supercritical CO₂ (ScCO₂) during the synthetic process. Due to the non-toxic and nonflammable nature of CO₂, ScCO₂ is a good solvent for the large-scale production of chemicals. The process is scalable and cost-efficient, and the ScCO₂ used can be recycled, which is ideal for industrial production. Indeed, this strategy was already used in several industrial processes such as food and pharmaceuticals.⁶⁹⁻⁷⁰ As CO₂ is non-polar, it is difficult to dissolve polar MOF precursors in pure ScCO₂. Thus, ScCO₂ is often used as a cosolvent in MOF synthesis. In 2014, Yang and

coworkers successfully utilized ScCO_2 with DMF for the synthesis of HKUST-1.⁷¹ By adopting this strategy, the team was able to modify the intrinsic porosity of the MOF, producing HKUST-1 with mesopores (13–23 nm). This work shows that the use of ScCO_2 not only facilitates MOF production, but also is able to improve the quality of synthesized products. Domingo and coworkers further demonstrated the use of ScCO_2 for the synthesis of a wide variety of MOFs, including MIL-88B(Fe) and ZIF-8.⁷² They greatly reduced the secondary solvent used, with only 2% v/v of dioxane employed, showing that ScCO_2 is a versatile and feasible method for the synthesis of MOFs in general. However, these studies were conducted on a milligram scale. Nevertheless, they lay the foundation for future work concerning MOF synthesis using ScCO_2 .

Despite its non-polar nature, ScCO_2 was also shown to be suitable as a solvent for MOF synthesis. Li and coworkers synthesized a series of ZIFs, including ZIF-8, with pure ScCO_2 (Fig. 9a and 9b).⁷³ Solid reagents were ball-milled and mixed together with ScCO_2 during the process to yield the MOF products. The reaction is highly efficient, taking only 5 min. The research team was also able to scale the reaction to produce ZIF-8 in a 100 g batch, further establishing the industrial relevance of this methodology. Recently, Novosselov and coworkers used a similar strategy to produce UiO-66 (Fig. 9c).⁷⁴ The flow set-up was used to mix $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ and terephthalic acid dissolved in DMF with preheated ScCO_2 for the rapid formation of crystalline products. 8.71 g of UiO-66 was produced in 5 min using the set-up, giving one of the highest production rates reported. Thus, these studies showed that it is viable to use ScCO_2 for the industrial production of MOFs.

A more important aspect of ScCO_2 is its use for MOF activation. The elimination of ScCO_2 from synthesized MOFs avoids liquid-gaseous transition, typical of other activation methods, to access the porosity of MOFs synthesized. This prevents the collapse of scaffolds and loss of porosity during the MOF activation process. This development was successfully

demonstrated by Matzger and coworker in 2013, when the team subjected a series of MOFs to ScCO_2 activation, including MOF-5, HKUST-1, MOF-74 and UiO-66.⁷⁵ The resultant MOFs show superior surface area and porosity as compared to conventional vaporization route. This method has a promising potential for the activation of MOFs that are more sensitive to activation conditions, opening up more MOF types for industrial production. As such, ScCO_2 is an important and promising tool for the large-scale commercialization of MOFs.

1.2.1.6 Mechanochemical Synthesis

Although the above-discussed methods are highly attractive, they inevitably involve the use of solvent. Recently, the rise of mechanochemistry offers a greener and more sustainable way for chemical synthesis.⁷⁶ By using mechanical energy to grind or mill precursors together, only a minimal amount of solvent is needed. In some instances, solvent can be eliminated completely, avoiding the cost for solvent purchase and waste solvent treatment during scaled up production. As such, this method is very attractive for industrial use. Mechanochemistry-based reactions are also highly efficient, typically take shorter time and lesser energy. As such,

Figure 10. (a) Synthetic scheme for the synthesis of HKUST-1, ZIF-8 and Al(fumerate) MOFs via mechanochemical extrusion. (b) Twin screw extrusion for the continuous production of UiO-66-NH₂. Reproduced with permission from ref 83 and 84.

adopting mechanochemical method for the synthesis of porous materials, such as MOFs, is an attractive option for their industrial production. Numerous reports for mechanochemical synthesis of MOFs (HKUST-1,⁷⁷ ZIFs,⁷⁸ MOF-5,⁷⁹ MOF-74,⁸⁰ UiO-66,⁸¹ UiO-67⁸² and NU-901⁸²) were found in the literature. Most of them are milligram scale reactions, establishing a strong foundation and serving as proof of concept for scaling-up production.

In 2015, James and coworkers reported large-scale syntheses of HKUST-1, ZIF-8 and Al(fumurate)(OH) by extrusion using a commercially available extruder (Fig. 10a).⁸³ The prepared materials were comparable with those synthesized from solvothermal method, proving that the quality of resultant MOF nanocrystals was not compromised using this new synthetic pathway. Similarly, Užarević and coworkers reported the manufacturing of zirconium-based MOFs (UiO-66, UiO-66-NH₂, MOF-801 and MOF-804) using twin screw extrusion technique (Fig. 10b).⁸⁴ By utilizing preformed dodecanuclear Zr acetate clusters as the precursor, multigram scale synthesis of zirconium-based MOFs was achieved by extrusion, with minimal amount of water added for liquid-assisted grinding. These studies show that it is possible to synthesize MOFs in a continuous fashion using mechanical extrusion method to achieve multigram scale production effectively. Compared to other synthetic methodologies, mechanochemical synthesis has one of the highest production rates. With little or no solvent used during the process, it is indeed a viable methodology to consider for the large-scale synthesis of MOFs. While scientists continue to search for viable and industrially relevant methods for MOF synthesis, more interesting results are expected from this direction of research, as we realize the potential of mechanical power in chemical transformation.

1.2.1.7 Dry Heating

While typical MOFs can be synthesized by mechanochemical milling alone, more chemically inert MOFs require harsher conditions for their formations. MIL series MOFs,

especially the Cr variation, are generally formed at elevated temperatures, with highly corrosive additives, such as hydrofluoric acid (HF).^{9, 85-86} To effectively scale-up the synthesis of these MOFs, it is crucial to eliminate the use of these harmful additives. A combination of grinding and heating allows for the elimination of both solvents and additives used in the synthetic procedure, making it an attractive option for the industrial production of such MOFs. In addition, the time taken for MOF formation is reduced as well, resulting in a more efficient synthetic process. Xu and coworkers successfully synthesized MIL-101(Cr) via a two-step grinding and heating method.⁸⁷ The method avoids the use of both solvent and corrosive HF additive, providing a greener and more sustainable route to MIL-101(Cr) production. The

Figure 11. (a) Proposed mechanism for the synthesis of ZIFs via dry heating. (b) Schematic representation for the production of various MOF-fabric composites via dry heating. Reproduced with permission from ref 88 and 89.

resultant materials were compared to solvothermal-prepared samples, with and without the use of HF additive, to show the feasibility of this method.

Apart from the MIL series MOFs, this method is also applicable to other MOF types as well. Recently, Chaemchuen and coworkers applied similar heating strategy for the production of ZIF-8 and ZIF-67 (Fig. 11a).⁸⁸ Precursors were heated at close to the boiling point of the organic linker, 2-methylimidazole, for a relatively short period of time (1 h). This process effectively removes excess reagents and eliminates the need for postsynthetic washing. Wang and coworkers also utilized this principle to directly incorporate MOFs onto textile fabrics (Fig. 11b).⁸⁹ MOF precursors were grinded and spread onto the surface of fabric materials, before subjecting the components to a hot press. The heating alone, without additional solvents used, allows MOFs to form on the fabric materials within a short time span of 10 min. A wide variety of MOFs (i.e., ZIF-8, UiO-66, MIL-53(Al) and MFM-300(In)) and fabrics (i.e., aramid, polyester and cotton) were utilized, showing that the process is very versatile. These studies show that this method is not just limited to Cr-based MIL but can also be used for other MOF types. Dry heating is still a growing area for research and more exciting progress is expected in the future.

1.2.2 From Powder to Materials

MOFs in their powder form pose several problems for their eventual utilization, such as difficulty in handling, as well as clogging of tubing. Thus, it is important to transform MOFs from their powdered form into functional materials. The end usage or practical application of the resultant materials is crucial for the development of fabrication techniques. This should be viewed as a continuation of scaled up industrial synthesis to realize usable functional materials for the commercial market.

1.2.2.1 MOF Inks and 3D Printing

Figure 12. (a) Photoluminescent of MOF inks for the detection of aromatic compounds. (b) Thermo-receptive MOF inks coated on a rod, subjected to different temperatures. (c) 3D-printed HKUST-1 with high mouldability and flexibility. Reproduced with permission from ref 91 and 92.

By mixing MOFs with polymers in a solvent, MOF inks can be obtained. Given the wide commercial availability of polymers, a physical mixture of the two precursors can be further fine-tuned based on the product requirements. Composite materials obtained from this process inherit properties from both components, allowing for the creation of functional materials suitable for practical uses. Typically, polymer-MOF composites can enhance MOF stability in air and water. As MOFs are synthesized reversibly via coordination bonding, the weak linkages are often susceptible to water, or even moisture in the air.⁹⁰ By combining a hydrophobic polymer with MOFs into a suspension, the resultant MOF inks can be stable to air and water, even when the pristine MOFs are not. Recently, Kim and coworkers prepared a MOF ink by mixing a fluoropolymer with MOFs.⁹¹ The ink was stable as a suspension, and a

coating can be achieved upon the evaporation of solvent. The coating exhibits high contact angle, indicating that the composites possess excellent hydrophobicity, and can be applied to a wide variety of surfaces. The authors further showed that this method can be applied to different MOF types, suggesting that this strategy is versatile. To probe the functionalities of the composites, two different types of MOF inks were prepared, deliberately using moisture sensitive MOFs as components. The resultant coatings possess chemical and thermal sensing properties imparted from their respective MOFs, while remaining stable in air due to the presence of the hydrophobic polymer (Fig. 12a and 12b). This study clearly illustrated the advantages of composite ink materials consisting of MOF and polymer constituents. This class of composite materials can be easily synthesized via physical mixing, showing the versatility and highly functional properties. It is important to keep in mind that fluoropolymers usually add on to the cost of MOF production as they are typically more expensive to be produced as compared to their non-fluorinated counterparts. A good solution would be to utilize non-fluorinated hydrophobic polymers in combination with MOFs to keep the price of the resultant materials competitive. In addition, adhesion to surfaces can easily be worn off, as there are no chemical linkages between the coating and surfaces. Nevertheless, this approach to generate MOF inks using hydrophobic polymers remains promising to give functional MOF composite materials.

MOF inks can also be utilized to build elaborated designs, with the help of 3D printing technology. Recently, a number of reports⁹²⁻⁹⁴ utilizing MOFs with different ink compositions illustrated the increasing interest in 3D printed patterns (Fig. 12c). This technique is applicable for a wide variety of MOF types (i.e., HKUST-1, ZIF-8, and UiO-66-NH₂) and the resultant products can be shaped into different morphologies using 3D printing. The composites obtained also showed a retention of inherent MOF properties, allowing for potential uses in practical applications. Rezaei and coworkers 3D-printed MOF-74(Ni) and UTSA-16(Co) with clay as

the binder for selective CO₂ adsorption.⁹⁵ High MOF loading of up to 85 wt.% can be achieved and the prepared materials can be used for at least 5 cycles with no decrease in their performance. Maya and coworkers successfully printed ZIF-67 MOF with polyvinylidene fluoride (PVDF) for the degradation of organic dye, i.e., rhodamine B.⁹⁶ 98% degradation was achieved within a short time frame of 10 min, having good reproducibility and recyclability. By designing suitable MOF-polymer mixed inks and using them for 3D printing, MOF-based composite products can be obtained easily on a large-scale. With the advancement in 3D printing technology, the cost is expected to decrease further in the near future, making it one of the most promising strategies to produce custom-made MOF-based composite products.

1.2.2.2 Mixed Matrix Membrane

Figure 13. (a) Fabrication of various flexible MMMs containing MOFs. (b) Schematic representation showing different types of MMMs obtained by distinct casting techniques. (c) HKUST-1 MMM exhibiting a color change upon exposing to a chemical warfare agent simulant (CEES). Reproduced with permission from ref 97, 98 and 99.

A combination of polymers and MOFs can also be casted into fixed shapes by traditional molding technique. The fabrication of mixed matrix membranes (MMMs) is one such examples. Cohen and coworkers successfully synthesized a series of MMMs by combining a variety of MOFs (i.e., UiO-66, MIL-101, HKUST-1, MIL-53, and ZIF-8) with PVDF polymer in DMF (Fig. 13a).⁹⁷ The team was able to achieve high loading of MOFs (~67 wt.%) onto the MMMs, granting flexibility and robustness to the powdered MOFs using a drawdown casting technique. This method is easily scalable, and the resultant membranes are moldable before casting. This work also demonstrated postsynthetic chemical functionalization of MOFs within MMMs, a major breakthrough in MOF-based MMMs. The as obtained products were also shown to be functional, possessing the ability for dye separation. The team further studied how this technique can be used by creating different types of MMMs, such as co-casted, mixed MOFs, and layered MMMs (Fig. 13b).⁹⁸ By combining MOFs and MMMs in different ways, they were able to show the versatility in creating a wide variety of useful MMM products. In co-casted MMMs, different membranes were casted side-by-side and elaborated patterns can be created with careful controls. Mixed MOF MMMs can be fabricated by introducing more than one type of MOF in the casting solution, granting them with multifunctional properties. In layered MMMs, multiple layers of MMMs can be stacked on top of one another. The prepared MMMs are effective for cascade catalytic reactions, utilizing two different MOFs in one MMM form for sequential reactions.

Several other research teams also demonstrated the effectiveness of MOF-based MMMs for different applications. Epps and coworkers showed the potential of HKUST-1 based MMM as a possible replacement for vinyl rubber personal protective equipment in the protection against sulfur mustard chemical warfare agent stimulant, 2-chloroethyl ethyl sulfide (CEES).⁹⁹ Not only is the MMM capable of adsorbing CEES vapor, preventing it from penetrating across the membrane, it also exhibits visible color change upon the exposure,

allowing for visual colorimetric detection of toxic CEES as well (Fig. 13c). The same team also fabricated a layered sandwich MOF MMM that allows for fine tuning of mechanical properties exhibited by the synthesized MMM.¹⁰⁰ The resultant MMM was utilized for the mitigation of nerve agents soman and VX. Sivaniah and coworkers showed that the MMM constructed from amine functionalized UiO-66-NH₂ was capable of CO₂ capture.¹⁰¹ The MMM was rationally designed for its intended purpose, with good porosity and selectivity, due to the presence of MOF and amine groups. MMMs are excellent composite materials readily derived from MOF powders via a simple mixing and casting procedure. They possess a tremendous potential to be developed into usable products, to address some of the real-world problems in modern time.

1.2.2.3 Electrospinning

Figure 14. (a) Electrospinning technique for various MOFs on nonwoven fabrics. (b) Feasibility of using electrospinning to coat gloves and face masks with MOFs. (c) Schematic illustration showing electrospinning process, followed by the carbonization of MOF-polymer composites for oxygen reduction reaction. Reproduced with permission from ref 104 and 105.

Another promising technique to prepare functional MOF-based materials is via the use of electrospinning. By applying a potential difference between the metallic needle and a target surface, MOF-polymer precursors in polar solvents can be attached to the surface via columbic attraction. Upon evaporation of solvent, a mixture of MOF and polymer would be left behind and casted onto the surface of the target.¹⁰² This technique allows for the facile coating of MOF-polymer composites onto surfaces and textiles. Kasfel and coworker demonstrated the feasibility of this technique in 2011.¹⁰³ The team investigated three polymer–solvent systems for electrospinning (i.e., polystyrene in tetrahydrofuran, polyvinylpyrrolidone in ethanol, and polyacrylonitrile in dimethylformamide), with two representative MOFs, namely HKUST-1 and MIL-100(Fe). High MOF loadings were achieved, giving 40 wt.%, 80 wt.% and 80 wt.% for the three systems respectively. The spun composite fibers retained good porosity and crystallinity, suggesting that the integrity of the MOF structures was not compromised after the electrospinning process. Wang and coworkers used a similar set-up to coat MOFs onto polymeric fibers (Fig. 14a).¹⁰⁴ The team extended the investigations to more MOFs, such as ZIF-8, UiO-66-NH₂, and MOF-74. Lower MOF loading at 60 wt.% was used, which may enhance the flexibility of the resultant filters. The filters were then used for the removal of particular matters in air (PM 2.5 and PM 10) and also tested for SO₂ dynamic adsorption, achieving remarkable results in both cases. The team further studied the feasibility of using this method for coating a layer of MOFs onto objects, such as gloves and face masks, showing the applicability of this technique for practical uses (Fig. 14b).

Electrospinning was also utilized to generate other functional materials for a wide variety of applications. Chen and coworkers adopted a two-step electrospinning-carbonization strategy to fabricate a highly doped electrocatalyst for oxygen reduction reaction (Fig. 14c).¹⁰⁵ The prepared material was low-cost and robust, outperforming commercially available 20 wt.% Pt/C electrode in oxygen reduction reaction. Wang and coworkers pyrolyzed the electrospun

ZIF-8 nanofibers to obtain a hierarchical carbon material enriched with N atoms.¹⁰⁶ The obtained material possessed excellent conductivity, while retaining the porosity of MOFs, making it suitable as a supercapacitor. Van der Voort and coworkers electrospun Pt@MIL-101 with polyacrylonitrile to give an effective catalytic carpet for the hydrogenation of cyclohexene.¹⁰⁷ A full conversion to cyclohexane was observed in 90 min, and the prepared material can be recycled up to four times, indicating its high efficiency as a catalyst. Lan and coworkers utilized MOF-808 and Basolite F300 to electrospin nanofibers for water treatment application.¹⁰⁸ The as-prepared composites are effective for the adsorption of toxic Pb and Hg ions from water. While electrospinning is good for generating nanofibers to be coated onto surfaces, there are several drawbacks associated with this technique. Similar to 3D printing, this technique requires the use of a specialized instrument, which adds to the cost of production upon scaling up. Furthermore, adhesion between the nanofibers and surfaces is physical in nature. Thus, the resultant coating may not be able to withstand abrasion and stress. Nevertheless, it is clear that materials produced from electrospinning are suitable for a wide variety of practical applications, suggesting that this is a powerful tool for the preparation of highly functional composites.

1.2.2.4 MOF Fabric

Most MOF fabric composites were generated via in-situ growth of MOF crystals onto fabric materials.¹⁰⁹⁻¹¹² While this approach might be appropriate for sample preparation in small scale laboratory setting, it is highly inefficient and not scalable from an industrial perspective. It is difficult to restrict MOF growth only to the fabric substrates, resulting in wastage during the fabrication process when some of the MOF particles nucleate in the synthesis solution

instead. At the same time, the fabrications are typically performed under solvothermal conditions, which take a long time for the preparation. Thus, it is more feasible to adopt a different strategy, namely, to bind pre-synthesized MOFs onto fibers. In 2016, Li and coworkers introduced a γ -radiation induced polymerization strategy to effectively bind MIL-101(Cr) onto nylon substrates.¹¹³ Upon irradiation, free radicals were generated by MIL-101(Cr), which initiated the polymerization of 2-hydroxyethyl acrylate added. The resultant composite materials were “dyed” yellow due to the presence of MIL-101(Cr) and can be subjected to dry cleaning conditions for reuse. While this is a scalable means to achieve MOF binding onto fabrics via a facile method, the use of high energy radiation dosage significantly limits the practical use of this strategy.

Figure 15. (a) Schematic illustration of post-synthetic modification of UiO-66-NH₂, followed by polymerization, to give MOF/nylon hybrid composite. (b) Schematic representation showing the dip coating process of MOF-808 onto cotton fiber using polyethylenimine as the binder. Reproduced with permission from ref 114 and 116.

Cohen and coworkers synthesized a UiO-66-NH₂/nylon composite based on a post synthetic polymerization strategy (Fig. 15a).¹¹⁴ Amide condensation reaction between adipoyl chloride and pendant amine group on UiO-66-NH₂ allows for surface modification of MOF substrates and their subsequent incorporation into the nylon polymer. This elegant strategy easily combines powdered MOF with nylon via covalent linkages and requires no additional materials. Therefore, it has high industrial relevance and can be readily adapted for nylon manufacturing process. The same team also demonstrated a similar strategy utilizing a modified UiO-66-NCS for post synthetic polymerization with polyamine substrates to yield a polythiourea composite.¹¹⁵ The resultant composite was spray-coated onto a common warfighting textile, Nyco, with great adhesion and compatibility. Both hybrid materials synthesized showed excellent degradation performance for nerve agent simulants and established themselves as suitable candidates for the fabrication of protective wearables.

The coating of textile using a binder/MOF solution has gathered significant attention. Farha and coworkers utilized a MOF/polyethylenimine suspension to dip-coat MOF-808 and UiO-66-NH₂ onto cotton fibers (Fig. 15b).¹¹⁶ Glover et al. utilized a MOF/ionic liquid suspension to coat UiO-66-NH₂ onto cotton fabrics.¹¹⁷ Several procedures were listed, such as direct-contact, airbrush spraying and yarn loading, demonstrating the versatility of this strategy. This method of coating is facile, efficient and readily scalable for industrial fabrication of textile materials. Furthermore, it could be applicable to a wide range of MOFs as there is no covalent interaction between the MOFs and the binders. On the other hand, it is possible that the binders used can interact with the MOFs and modify the properties of the resultant porous materials. The cost of the binders used should also be taken into consideration for this strategy to be applied industrially. In general, as we are only starting to explore this strategy, more studies need to be conducted to better understand the properties of these composite materials.

1.2.2.5 Foams and Aerogels

Figure 16. (a) MOF foam synthesized from MOF-alginate mixture, exhibiting exceptional strength and toughness. Characterization data show that ZIF-8 is embedded within the composite. (b) Various MOF bead composites synthesized from alginate and polyacrylic acid mixture. (c) Schematic diagram showing the fabrication of ZIF-sponge composite via surfactant-mediated coating. Reproduced with permission from ref 121, 122 and 125.

Alternatively, MOFs can be combined with natural polymers, such as cellulose and gelatin, to give foams and aerogels. Freeze-drying technique is often utilized for the synthesis of these types of materials, with direct sublimation of solvent molecules. This process is scalable and has been used in various industries, such as food and pharmaceuticals.¹¹⁸⁻¹¹⁹ The resultant products often possess hierarchical porous structures and can be molded into various morphologies depending on the shapes of the containers used. Zhu and coworkers fabricated aerogels by combining cellulose with MOFs such as ZIF-8, MIL-100(Fe) and UiO-66.¹²⁰ Their studies showed that the MOF particles were embedded in a network of cellulose. The highly porous and flexible products also exhibited remarkable Cr(VI) ion adsorption capability from

aqueous solution. Wang and coworkers also synthesized a series of foams based on MOF-alginate composites by a similar process.¹²¹ The team used ZIF-8, UiO-66, UiO-66-NH₂, MIL-101-NH₂ and MOF-74(Zn) for the synthesis of these foam products, showing the versatility of their method. This study shows that it is easy to modify the resultant shapes of the fabricated composites via the use of scaffolds before the freeze-drying process. Layered foams consisting of different types of MOFs can also be achieved during the process. The as-prepared materials showed high tensile strength, which were suitable for practical uses (Fig. 16a). These foams were used as filter substrates for the adsorption of toxic AsO₄³⁻ ion and particulate matters (i.e., PM2.5 and PM10), showing remarkable properties in these applications.

Recently, Queen and coworkers successfully synthesized a series of MOF-alginate-polyacrylic acid composites via a gelation and freeze-drying protocol.¹²² The introduction of polyacrylic acid greatly improved the mechanical strength of the resultant composites. Their strategy can be applied to a wide variety of MOF types (Fig. 16b) to give functional bead products. One of the composites containing Fe-MOF showed remarkable Pb and Pd adsorption in aqueous condition, which is promising for water purification purposes. Martyanov and coworkers synthesized a HKUST-1 silica aerogel composite for molecular separation application.¹²³ The study showed that it is possible to control the HKUST-1 to silica content through a sol-gel preparation method, enabling resultant composites with various HKUST-1 loadings. The prepared materials were immobilized as the stationary phase in a liquid chromatography column, allowing for the effective separation of cyclohexane from cyclohexene. Yamauchi and coworkers utilized a green and efficient methodology to create an ultralight aerogel containing ZIF-8, with agarose as the binder.¹²⁴ The resultant material demonstrated high adsorption capacity for organic solvents and common oils. It also has excellent recyclability, which is crucial for its practical utilization as an adsorbent for organic pollutants.

Apart from freeze drying, dip coating is also a popular method to introduce MOFs onto a solid scaffold, such as sponge materials. Chang and coworkers successfully embedded ZIF-67 onto surfactant-modified melamine sponges (Fig. 16c).¹²⁵ The team proposed that the combination of electrostatic and π - π stacking effects led to the accumulation of MOFs on sponge surfaces. The composite materials showed effective removal of malachite green, a toxic pollutant, from aqueous solution. The facile coating of MOFs onto robust materials, such as melamine sponge, allows for the use of the resultant systems in practical applications. Recently, Park and coworkers made a MOF-sponge composite, containing HKUST-1 and MIL-160, by a squeeze coating method.¹²⁶ The resultant products contained various loading of MOF precursors (10–39 wt.%), and showed good gas sensing selectivity for H₂ and CO, even in the presence of humidity. In situ polymerization represents another effective method for the preparation of foams and sponges. Monomers and MOF precursors are mixed together before the polymerization is initiated to give a MOF-polymer composite. Blight and coworkers fabricated a MOF-sponge composite using a co-polymerization technique with pre-synthesized Zr-based MOF-808.¹²⁷ The MOF loading was 25 wt.%, and the composite was shown to be effective for the hydrolysis of chemical warfare agent VX. Adapting existing processing technologies, such as freeze drying and dip coating, to the development of MOF foams and sponges is an effective way of generating functional MOF composites. The resultant foams and aerogels are important classes of functional materials with a great potential to address some of real-world problems.

1.3 Thesis Objectives

Given the versatility and unique properties of MOFs, it is likely for them to have impact beyond the scientific community, as possible solution for real-world problems. While numerous studies after 2 decades of research have shown great potential for MOF as functional materials, progress in MOF commercialization is still relatively slow. Two major roadblocks impeding the progress are the production and processability of MOFs.¹²⁸

While a large number of MOFs exists in the scientific literature, only few MOF types, predominantly those with affordable and commercially available organic linkers, are produced on a large-scale. Designer linkers derived from multistep synthesis often bear high cost of production and are often only available on a laboratory scale without proper procedure for scaling up. This renders the industrial production of most designed MOFs impractical. Apart from this, MOFs that are produced on a large-scale also face a magnitude of problems, ranging from the high cost of production to quality control. The main issue in translating from small scale to larger scale production is the lack of suitable synthetic methods. Most MOFs are made via solvothermal synthesis, under high temperature and over a long duration of time. Therefore, it is necessary to address this issue to facilitate large-scale production of MOF products.

MOF products typically exist as fine powder after synthesis. For them to translate into useful products, they must be shaped or integrated with existing materials. This poses a new set of challenge for post-production, as some industrial processes to treat powdered sample compromise the quality of MOFs prepared. For example, pelletization of HKUST-1 under pressure resulted in significant decrease in porosity due to the weak mechanical property of the MOF itself.¹²⁹ Clogging of pore space could also undermine the performance of MOF materials when they are physically mixed with another material. Although efforts to develop MOFs into useful products, such as cloth,¹⁰⁴ foams¹³⁰ and ink¹³¹ etc., are currently on its way, it still

remains a relatively unexplored area of research till date. Thus, it is a huge challenge to find innovative solution to transform MOF from its powder form, into usable and practical products.

In this thesis, method development for the synthesis of MOFs and processing of MOF into usable functional materials will be systematically investigated upon (Fig. 17). Several important key parameters, such as practicality, cost efficiency and scalability, will be used to evaluate the feasibility of the work presented. This work hopes to bridge the gap between academia and industry to realize MOF potential for real-world uses.

Figure 17. Schematic presentation of the route to MOF commercialization. Reproduced with permission from ref 128.

In chapter 2, the development of a solvent- and HF-free methodology to synthesize flexible chromium-based MOFs, MIL-53 and MIL-88B, will be described. Pure phase MIL-53 and MIL-88B can be obtained selectively by using different metal salt precursors and were characterized extensively. This work provided a greener synthesis condition for the development of large-scale production for MIL-53 (Cr) and MIL-88B (Cr).

In chapter 3, the development of a facile methodology to embed as-synthesized MOF powder onto fabric substrates to form a MOF-fabric composite will be illustrated. Through the use of poly(acrylic acid) as binder, MOF-fabric composite can be easily fabricated by dripping the MOF/polymer suspension onto fabric directly, followed by a drying process. This process is fast, with minimal waste produced and it is applicable for different types of MOFs and fabric materials. The as-prepared MOF/fabric and MOF/mask composites are shown to possess superior antimicrobial properties due to the MOF embedded. This methodology has the

potential to be used in the development of usable personal protective wearables for healthcare workers.

In chapter 4, the development of a gram-scale synthetic method for ZIF-8 MOF and its subsequent coating onto cotton fabric will be discussed. The unique features of this synthetic protocol are low temperature, high yield and instantaneous production of high-quality ZIF-8 nanoparticles. This facile methodology can be easily adapted for large-scale synthesis. The as-prepared ZIF-8 powder was coated onto cotton fabric using polystyrene binder to give ZIF-8/cotton-40mg composite. ZIF-8/cotton-40mg showed superior dye absorption capability for both cationic rhodamine B and anionic methyl orange as compared to PS/cotton control. Also, the composite possesses enhanced antibacterial properties as well. These show that the coated ZIF-8 retains its unique properties upon postsynthetic modification. By considering both production and processing, this project illustrated a feasible pathway for the industrialization of ZIF-8 and ZIF-8-based composites.

In chapter 5, a brief summary of all work done will be provided and their contribution to the bigger picture of MOF industrialization will be elaborated upon. Future direction in which these projects can be further develop will also be discussed.

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Chapter 2

Solvent- and HF-Free Synthesis of Flexible Chromium-Based MIL-53 and MIL-88B

2.1 Introduction

Solvent waste contributes significantly to the cost in an industrial process. Large quantity of solvents used for chemical production needs to be properly treated before disposal, especially when harsh chemicals, such as hydrofluoric acid (HF), were used during the synthetic process. A good approach to address this is to consider developing synthetic strategies based on green chemistry. Not only is this economical, but it is also sustainable in the long run. Hence, it is not surprising that green synthesis of MOFs has garnered significant attention in the community recently,¹⁻² which has tremendous impact on the large-scale commercialization of MOF products.³⁻⁴

Flexible MOFs are particularly interesting, due to their ability to “breathe” or “swell” under different stimuli without a permanent irreversible destruction in the framework structures.⁵ Two of the earliest MOFs found to display such breathing effect were the chromium variants of MIL-53 and MIL-88 (MIL stands for Material Institute Lavoisier). Discovered in 2002 by Férey and co-workers,⁶⁻⁷ MIL-53 (Cr) was found to possess extensive breathing effect when subjected to various temperature and solvent conditions. The inorganic building units are made up of corner-sharing chromium octahedra joined together via μ_3 -OH bridging units. The inorganic component is able to combine with terephthalate units to give a 3-dimensional flexible framework. Isomorphous to MIL-53 (Cr), MIL-88B (Cr) was first reported by the same group in 2006.⁸ Unlike MIL-53 (Cr), terephthalate spacers in MIL-88B (Cr) are connected by the trichromium μ_3 -O inorganic building units. While MIL-53 (Cr) was widely studied, MIL-88B (Cr) was less known, due to a lack of clear synthetic protocol to produce the material itself.⁹⁻¹⁰ This crucial synthetic challenge should be addressed in order to explore the potential

application of MIL-88B (Cr). In addition, these two MOFs are usually synthesized by hydrothermal methods, with HF as an acid modulator. In order to scale up the production and eventually commercialize these MOF products, there is a need to explore safer and greener methods to prepare these MOFs without the use of corrosive HF and bulk solvents.

In recent years, several studies on solvent-less and HF-free synthesis of MOFs from the MIL series have been reported, including the synthesis for MIL-100 (Fe),¹¹ MIL-100 (Cr),¹² and MIL-101 (Cr).¹³ In this study, MIL-53 (Cr) and MIL-88B (Cr) had been successfully synthesized without the addition of both solvent and HF (Scheme 1). The synthetic procedure is highly selective based on the type of chromium salt used, and the synthesis could be carried out in a relatively shorter duration of time as compared to conventional hydrothermal method. This is, to the best of our knowledge, the only reported protocol that gives pure phase chromium-based MIL-88B. The synthesized samples were fully characterized by multiple techniques to demonstrate that they were isomorphous MIL-88B (Cr) and MIL-53 (Cr). By eliminating the use of solvents and HF in the synthetic protocol, this work brought us a step closer to the large-scale production of flexible MOF products.

Scheme 1. Solvent- and HF-free synthesis of Cr-based MIL-88B and MIL-53.

2.2 Experimental Section

2.2.1 Materials and Characterizations

All reagents and solvents are commercially available and were used without further purifications. Powdered x-ray diffraction (PXRD) experiments were carried out at 40 kV and 15 mA, with a Cu-K α radiation over a 2θ range of 5°–50°, using a Rigaku MiniFlex 600 benchtop diffractometer at room temperature. Thermogravimetric analysis (TGA) was carried out with a heating rate of 10°C/min under air flow (60 mL/min) from 30°C to 800°C, using a TGA TA Instrument 2950. Gas sorption studies were conducted using Quantachrome Instruments Autosorb-iQ with pure N₂ gas at 77 K. Brunauer-Emmet-Teller (BET) surface areas were calculated by predetermined adsorption points measured, using the micropore BET assistant function in the Quantachrome ASiQwin software. Fourier transform infrared (FTIR) spectra were recorded in attenuated total reflectance (ATR) mode using a Perkin-Elmer 100 FTIR spectrometer. Scanning electron microscopy (SEM) images were taken using a JEOL JSM-7600 field emission scanning electron microscope operating at 5.0 kV. X-ray photoelectron spectroscopy (XPS) experiments were carried out using a SPECS Hemispherical Energy Analyzer Series PHOIBOS 100/150 with a Mg K α X-ray source.

2.2.2 Synthesis and Activation of MIL-88B (Cr)

Cr(NO₃)₃·9H₂O (1.2 g, 3 mmol) was mixed with benzene-1,4-dicarboxylic acid (0.33 g, 2 mmol). To ensure thorough and controllable mixing, the solid precursors were mechanically mixed using a commercial ball-mill grinder (Retsch MM-400) at 30 Hz for 30 min in a 15 mL snap-on FTS-1000 milling jars loaded with a 10 mm stainless steel ball bearing. The resultant powder was kept as a stock mixture before it was used in the next step. The mixed powder (0.7 g) was then heated in a 20 mL Teflon-lined autoclave at 190°C for 3 h. The resultant slurry was washed with EtOH before it was dried in an 80°C oven overnight to obtain MIL-88B (Cr).

as a green powder (0.19 g, 50.8% based on terephthalic acid used). For optimization, the amount of mixed powder loaded (0.7/1.2/2.3 g) and temperature of synthesis (160°C/190°C/220°C) were varied accordingly in this procedure.

2.2.3 Solvent Exchange Experiment for MIL-88B (Cr)

As-synthesized MIL-88B (Cr) was dispersed and soaked in MeOH, before the suspension was centrifuged to remove the MeOH supernatant. The resultant solid was dried briefly under N₂ gas and was immediately subjected to PXRD analysis to reduce solvent loss from the pores. The analyzed powder was then dispersed and soaked in H₂O before the suspension was centrifuged to remove the supernatant. The resultant solid was dried in an 80°C oven before PXRD analysis again.

2.2.4 Synthesis and Activation of MIL-53 (Cr)

The procedure was identical to section 2.2.2 except that CrCl₃·6H₂O (0.8 g, 3 mmol) was used instead. The heating was maintained for 15 h and the obtained sample was washed using deionized water and dried in an 80°C oven overnight to give a purple powder (0.20 g, 62.1% based on terephthalic acid used). The resultant product was further calcinated at 300°C under Ar for 30 h to produce the green activated form.

2.3 Result and Discussion

2.3.1 Powdered X-Ray Diffraction (PXRD)

Figure 1. (a) PXRD pattern of grinded sample compared to starting materials. (b) PXRD pattern of heated sample compared to grinded and simulated pattern.

To eliminate the use of solvent in the synthesis, an alternative method is required to mix the reagents homogeneously. Grinding is an attractive option to reduce particle size of reagents to achieve effective mixing. It is readily scalable and compatible for industrial production as well. Chemical reactions can also occur upon grinding, a process known as mechanochemistry.¹⁴ Several studies have already shown that MOFs can be synthesized via a mechanochemical process.¹⁵⁻¹⁷ Therefore, it would be worthwhile to grind the reagents together for homogeneous mixing in the absence of any solvent.

To check if any mechanochemical reaction has occurred during the grinding step, PXRD analysis was carried out to identify if there are any new crystallography phase in the grinded sample. Comparing the diffraction pattern of the grinded sample with the two individual starting materials (BDC and $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$), there is no significant change observed, suggesting that no mechanochemical reaction has occurred during the grinding step (Fig. 1a). This is likely due to the inert nature of $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ used, which typically requires elevated temperature for the formation of Cr-based MIL MOFs.^{7-8, 18} Thus, the grinded sample was further subjected to heating. Upon heating the mixture for only 3h at 190°C, a change in

Figure 2. (a) PXRD patterns of synthesis with different temperatures. (b) PXRD patterns of synthesis with various loading amount.

the diffraction pattern was observed for the resultant solid obtained (Fig. 1b). The new diffraction pattern matches that of MIL-88B (Cr), suggesting that the solventless and HF-free reaction proceed only after heating. It is worth mentioning the significance of this result. In contrast to the Fe analogue of MIL-88B, The Cr variation of MIL-88B has not been well reported. This is largely due to the ambiguity in the synthesis procedure. The method for synthesizing MIL-88B (Cr) was omitted from the original article published by Férey and co-workers.⁸ Only recently, a benzoic acid modulated strategy was reported to synthesize MIL-88B (Cr).⁹ But the synthesized material was shown to contain benzoic acid precursor within the MOF pores, which required activation at high temperature for its removal. In comparison, our method does not utilize any modulator to scaffold the construction of the framework. Hence, to the best of our knowledge, this is the first time in which pure MIL-88B (Cr) was obtained using such a facile and efficient method.

The temperature for synthesis was then optimized. As observed, 190°C was the optimal synthetic temperature for the reaction (Fig. 2a). At lower temperature (160°C), white crystalline product with diffraction pattern identical to the starting material, BDC, was obtained. No observable MIL-88B (Cr) peaks was recorded, suggesting that reaction does not proceed or

Figure 3. (a) PXRD pattern of grinded sample compared to starting materials. (b) PXRD pattern of heated sample compared to grinded and simulated pattern.

proceed at a very slow rate with lower temperature. At higher temperature (220°C) the material obtained was of significantly lower crystallinity. Thus, it would be best to prepare MIL-88B (Cr) using the original conditions; 190°C for 3h.

To show the feasibility of this method for upscale production of MIL-88B, the amount of grinded precursors loaded was increased from 0.7 g to 2.3 g. The increase loading does not seem to affect the PXRD peaks of the resultant samples (Fig. 2b), which suggests that this procedure is independent of the loading amount. Thus, this shows that the procedure can be readily scaled up for the large-scale preparation of MIL-88B(Cr) products.

The metal salt used was also varied to see if there is any change to the reaction. An alternative metal precursor, $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, was used to replace $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, following the optimized procedure. Similar to the previous case, grinding alone cause no significant change in the diffraction pattern of the resultant sample (Fig. 3a). The grinded sample was then subjected to heating. When the heating process was carried out for only 3 hours, crystalline BDC was the major component of the isolated product. This differs significantly from the experiments conducted using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the metal precursor. Upon heating for a longer period of time, diffraction peaks of BDC decreases from the isolated product and new

crystallographic phases emerged. After 15 h of heating, BDC peaks completely disappeared, leaving only the new crystallographic phases. The new PXRD patterns matched with that of isomorphous MIL-53 (Cr) (Fig. 3b).

By using an alternative precursor, a different product was obtained. This solvent- and HF-free synthetic methodology was shown to be highly selective based on the metal salt used. With $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$, only MIL-53 (Cr) was obtained and with $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$, only MIL-88B (Cr) was obtained. It is possible that the anions present in the Cr salts have a templating effect during the synthesis of the two MOFs. Therefore, further study could be carried out to elucidate the mechanism behind the selectivity behind MIL-88B (Cr)/MIL 53(Cr) formation.

2.3.2 Swelling of MIL-88B (Cr)

Scheme 2. Swelling of MIL-88B (Cr) upon solvent inclusion.

Figure 4. PXRD pattern of MIL-88B (Cr) undergoing solvent exchanged.

MIL-88B (Cr) was known to “swell” in the presence of polar solvents such as MeOH (Scheme 2). To test for this characteristic trait, the as-prepared MIL-88B (Cr) was subjected to solvent exchange to induce framework “swelling”. Incubation of the prepared MOF in MeOH gave similar diffraction peaks as those reported,¹⁹ suggesting an expansion of the flexible framework to incorporate the exchanged solvent molecules (Fig. 4). Subsequent incubation of the expanded framework in water gave a diffractogram identical to the pristine material, indicating that this process is reversible. The experimental results agree well with the findings from Férey and co-workers,¹⁹ supporting the conclusion that MIL-88B (Cr) was formed.

2.3.3 Calcination and Activation of MIL-53 (Cr)

Figure 5. PXRDs of MIL-53 (Cr) (a) before and (b) after calcination. Insets show the change in sample color upon calcination.

In order to study the properties of MIL-53 (Cr) prepared, pristine sample was activated at a high temperature to remove the BDC residue trapped within its pores. Upon calcination, the color of the sample changed from pale purple to pale green. Also, the PXRD pattern of the activated sample matched with the hydrated form (*i.e.*, MIL-53lt) of MIL-53 (Cr), indicating the successful removal of BDC residue from the sample (Fig. 5). This is comparable to a similar activation process done by Férey and co-workers,⁶ further confirming that the product obtained was MIL-53 (Cr).

2.3.4 Scanning Electron Microscopy (SEM)

Figure 6. SEM images of (a) MIL-88B (Cr) and (b) MIL-53 (Cr).

Well defined crystals were observed from SEM images of MIL-88B sample (Fig. 6). Crystal size vary significantly, showing hexagonal microrods of different length and width. The relatively small size of the crystals obtained resulted in peak broadening observed in the PXRD pattern. In addition, the non-uniform growth of the crystals also gives rise to the difference in relative peaks intensities as compared to the simulated pattern. Crystal morphology of the prepared sample is identical to the solvothermal synthesized sample of MIL-88B (Fe) reported in the literature,²⁰ suggesting the formation of MIL-88B framework.

SEM image of MIL-53 (Cr) also shown that the sample consist of rod-like crystals. Similar to the MIL-88B sample, they have various length and width, resulting in difference in relative peaks intensities and broadening of PXRD peaks, as measured previously.

2.3.5 X-Ray Photoelectron Spectroscopy (XPS)

Figure 7. XPS spectra for MIL-88B (Cr).

As stainless-steel grinding jars were utilized to mix the solid reactants together prior to the heating step, it is possible for Fe from the grinding jar to be incorporated into the resultant framework structures even when Fe-based salt was not used as the precursor. Thus, it is important to establish the identity of the metallic component in the products synthesized. By using XPS, the identity of the metallic species within the framework can be determined.

XPS scan of the MIL-88B sample from 570 eV to 590 eV gives 2 distinct peaks at 576.4 eV and 585.8 eV, corresponding to Cr 2p_{3/2} and Cr 2p_{1/2} respectively (Fig. 7a). This suggests the presence of Cr in the MIL-88B sample. Scan from 700 eV to 740 eV shows no observable signal, suggesting the absence of Fe in the MIL-88B sample (Fig. 7b). This supports the conclusion that the sample obtained was made of pure Cr without any Fe contamination from the grinding jars.

Figure 8. XPS spectra for MIL-53 (Cr).

Similar to the MIL-88B specimen, XPS scan of the MIL-53 sample from 570 eV to 590 eV gives 2 distinct peaks at 576.7 eV and 586.4 eV, corresponding to Cr 2p_{1/2} and Cr 2p_{3/2} respectively (Fig. 8a). This suggests the presence of Cr in the MIL-53 sample. Also, the scan from 700 eV to 740 eV shows no observable signal, suggesting the absence of Fe in the MIL-88B sample (Fig. 8b). Therefore, like the MIL-88B sample, the MIL-53 specimen obtained was also made of pure Cr without any Fe contamination from the grinding jars.

2.3.6 N₂ Adsorption and Desorption

Figure 9. (a) N₂ isotherm for MIL-88B (Cr). (b) Pore distribution analysis for MIL-88B (Cr).

N₂ isotherms were obtained to determine the intrinsic porosity of the prepared samples. By measuring N₂ adsorption and desorption using our prepared MIL-88B (Cr) and MIL-53 (Cr), insights regarding the interior pore regions can be evaluated and compared against literature data.

The N₂ isotherm for MIL-88B (Cr) shows that the material formed has negligible N₂ sorption (Fig. 9a). This is similar to the N₂ isotherm measured by Liu and co-workers⁹ after their sample was heated at 350°C under vacuo to remove the benzoic acid modulator trapped within the porous structure. The Brunauer-Emmet-Teller (BET) surface area calculated was 42.8 m²/g, which is also comparable to the value reported (~70 m²/g). Pore distribution analysis also suggests the absence of any form of pores within the framework (Fig. 9b). This can be rationalized as MIL-88B (Cr) exhibiting a ‘closed’ pore phase when solvent molecules are removed under degassing condition, which prevent the entry of N₂ gas molecules into the porous framework during the gas sorption measurement. N₂ absorption and desorption is likely to occur only on the surface of the nanoparticles and not within the porous structure due to the narrow pore region that exclude any form of physisorption.

Figure 10. (a) N₂ isotherm for MIL-53 (Cr). (b) Pore distribution analysis for MIL-53 (Cr).

Scheme 3. Expansion and contraction of MIL-53 (Cr) due to change in pressure.

The N₂ isotherm for MIL-53 (Cr) significantly differ from that of MIL-88B (Cr). N₂ adsorption was observed, and the desorption curve was noticeably different from the absorption curve at the low pressure region (Fig. 10a). While this is unusual for a typical porous material, where the adsorption and desorption curves are similar to each other, it is a characteristic feature of MIL-53 (Cr).²¹ Difference in pressure caused flexible MIL-53 (Cr) to expand and contract (scheme 3), resulting in N₂ sorption profile that deviates from conventional non-flexible porous material. The BET surface area calculated was 996.6 m²/g, comparable to reported value of 915 m²/g. Pore distribution analysis suggest the presence of micropores with half pore width of approximately 7 Å (Fig. 10b). From the N₂ sorption study, the porous and flexible nature of MIL-53 (Cr) synthesized was clearly observed.

2.3.7 Attenuated Total Reflectance – Infrared Spectroscopy (ATR-IR)

Figure 11. ATR-IR spectrum of (a) MIL-88B (Cr) and (b) MIL-53 (Cr).

Infrared spectrum of both MIL-88B (Cr) and MIL-53 (Cr) (Fig. 11) are comparable to those reported in the literatures,^{6, 8} further supporting the successful formation of the 2 flexible MOFs. Intense peaks from 1400-1700 cm⁻¹ are due to the presence of unsaturated C=C and C=O vibration from BDC organic linker and presence of broad peak across 3000-4000 cm⁻¹ is due to H₂O or -OH moieties attached to the Cr centers.

2.3.8 Thermogravimetric Analysis (TGA)

Figure 12. TGA curves for (a) MIL-88B (Cr) and (b) MIL-53 (Cr).

TGA curves for both specimens (Fig. 12) are similar and correspond well with previous literature reports.⁶⁻⁸ Initial decrease in weight is due to the loss of adsorbed water molecules as these MOFs are stored in air. Both species decompose at approximately 400°C, as indicated by the sharp decrease in mass around that region. This shows that both MIL-88B (Cr) and MIL-53 (Cr) have high thermal stability, suitable to be used for practical applications.

2.4 Conclusion

In this project, syntheses of two isomorphous Cr-based MOFs, MIL-88B (Cr) and MIL-53 (Cr), were presented. Their syntheses were carried out without using additional solvents and hazardous HF modulator, both of which are typically required for the synthesis of Cr-based MIL-type MOFs. The synthesized samples were fully characterized by multiple techniques to confirm that they were isomorphous MIL-88B (Cr) and MIL-53 (Cr). Synthetic procedure that gives MIL-88B (Cr) was established for the first time, allowing future exploration of its unique properties as well as potential applications. By eliminating the use of solvents and HF in the synthetic protocol, this work brought us a step closer to the large-scale production of flexible MOF products.

2.5 References

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Chapter 3

Facile Preparation of Anti-Bacterial MOF-Fabric Systems for Functional Protective Wearables

3.1 Introduction

In the previous chapter, the focus is on developing potential methodology for the scaled-up production of MOF powder. The next step towards commercialization of MOF products would be to improve processability of the prepared powder. MOFs as microcrystalline powders pose several problems for their utilization, such as difficulty in handling and contamination/clogging of pipelines.¹⁻² Till date, it is still a challenge to shape MOF powders into dense pellets as surface area and porosity of some MOFs decrease under high pressure during the pelletization process.³⁻⁵ This reduces the effectiveness of the resultant pellets for practical usage. Several other methods to shape MOFs were also developed, to obtain 3D printing ink,⁶⁻⁸ sponge,⁹⁻¹¹ aerogel,¹²⁻¹⁴ membranes¹⁵⁻¹⁶ and fabrics.¹⁷⁻¹⁸ In recent years, MOF fabrics have gained significant attention due to their potential for a wide number of practical usages.¹⁹⁻²⁰ They can be made into components of protective wearables, such as mask filters, clothing etc., for the mitigation of harmful chemicals or biological species. Huang et. al. synthesized a HKUST-1@chitosan non-woven fabrics via a dip-coating method.²¹ The prepared material was shown to be useful against sulfur mustard (HD). Similarly, Farha and co-workers coated Zr-based MOFs UiO-66-NH₂ and MOF-808 onto fabric material, allowing for the hydrolysis of nerve agents.²²⁻²³ Reynolds and co-workers have grown Cu₃(NH₂BTC)₂, a HKUST-1 analog, onto surface modified cotton substrate using a dip-coating method.²⁴ The prepared fabric composite shows anti-bacterial properties and is promising as protective wearables for healthcare workers. Wang et. al. incorporated ZIF-8 into non-woven fabric, to be made into face mask.²⁵ The resultant product is capable of photocatalytic degradation of bacterial species, as well as PM_{2.5} and PM₁₀ particulate removal.

Despite these promising studies, the development of MOF-fabric composite is still at its infancy. Most MOF-fabric composites are conventionally prepared by growing MOF onto fibers under solvothermal process. Typically, fabrics were immersed in solution containing precursors and heated for a fixed duration.^{23, 26-27} This is not practical for the large-scale production of MOF-based fabric materials. Also, this method does not limit MOF growth to the fabric substrate solely, as MOF powder nucleates in the synthetic solution as well. Furthermore, effective control over the quantity of MOF loaded was rarely demonstrated and most studies were also limited in their scope, as techniques were not shown to be applicable to a wide range of MOFs and fabric materials. A better alternative would be to anchor pre-synthesized MOF powders onto fabric material. In this way, we can have more control over various aspects of the coating process.

With advancement in biomedical science and healthcare, the need for functional materials to keep us safe from microbes is a pressing concern for humanity. In light of the recent COVID-19 pandemic, it is even more crucial to develop new functional protective wearables with anti-microbial properties to sufficiently eliminate biohazardous threats that medical professionals faced.²⁸ The incorporation of functional MOF into protective wearables is a promising strategy to address this problem.^{25, 29-30} Due to the customizability of MOFs, they can be strategically designed and optimized for the targeted killing of harmful microbials.³¹ In addition, their porous nature can also be utilized to encapsulate other antimicrobial molecules, making them more effective as the next generation of smart biomaterial.³² It is crucial for MOFs to be tightly bounded to these protective wearables to avoid the detachment of MOF during practical usage. Thus, strong adhesion between MOF and fabric substrates is an essential prerequisite to be considered during material design and construction. In this study, we have demonstrated a facile and general strategy for the production of MOF-fiber composites by drip casting a mixture of MOF and poly(acrylic acid)

(PAA) onto fabrics (Scheme 1). The amount of MOF loaded was well controlled by adjusting the MOF-PAA mixture and the as-prepared fabrics were easily dried after the treatment to give functional MOF-fabric composites, capable of eradicating bacterial strains. This novel method is versatile and can be applied to a wide range of MOF and fabric materials. Due to the PAA added, MOF and fabric are strongly bounded together to give a material suitable for use as protective wearables (eg. clothing and mask). The preparation of composite materials can be done in a short time span, allowing for rapid production to be carried out effectively. This efficient method could be easily scaled for the industrial production of highly functional MOF-based products. To the best of our knowledge, this unprecedented methodology addressed most of the common shortfalls associated with the commercial production of MOF-fabric composites, providing a simple and elegant solution to generate functional materials with real-world applications.

Scheme 1. Preparation of MOF-Fabric Composite.

3.2 Experimental Section

3.2.1 Materials and Characterizations

All reagents and solvents are commercially available and used without further purification. $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$ (>99%), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (99%), acetic acid (>99%), poly(acrylic acid) (average Mw ~1800), Benzene-1,4-dicarboxylic acid (98%) were purchased from Sigma-Aldrich. HF (48% in H_2O) was obtained from Merck. $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (AR grade) and trimesic acid (AR grade) were obtained from Sinopharm chemical reagent co. ltd. NaOH (AR grade) was obtained from VWR chemicals. ZrCl_4 was obtained from Shanghai Aladdin Bio-Chem. Textile and face mask were obtained from commercial sources. Powdered x-ray diffraction (PXRD) was carried out with a Cu-K α radiation (40kV, 15mA) over a 2θ range of $5^\circ - 50^\circ$, using a Rigaku MiniFlex 600 benchtop diffractometer at room temperature. Baselines were zeroed using JADE5 software. Thermogravimetric analysis (TGA) was conducted by heating the weighted sample at $10^\circ\text{C}/\text{min}$ under N_2 flow (60 mL/min) from 30°C to 800°C , using a TGA-Q500 Thermoanalyzer. Gas sorption studies were carried out using Quantachrome Instruments Autosorb-iQ with pure N_2 gas. Brunauer-Emmet-Teller (BET) surface area was calculated from the isotherm using absorption data points between 0.05-0.2 P/P_0 for comparison between samples. Fourier transform infrared (FTIR) spectra were recorded in attenuated total reflectance (ATR) mode using a Perkin-Elmer 100 FTIR spectrometer. Scanning electron microscopy (SEM) and energy-dispersive x-ray spectroscopy (EDX) images were taken with a JEOL JSM-7600 field emission scanning electron microscope operating at 5.0kV. EDX was carried out using the same equipment at 15.0kV.

3.2.2 Density Functional Theory (DFT) Calculation

All calculations were conducted on the Vienna ab initio simulation package (VASP 5.4.4) and the exchange and correlation functional was treated as the generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) formula. The periodic HKUST-1 structure, HKUST-1-PAA, HKUST-1-glucose, and HKUST-1-PAA-glucose were optimized and their ionic positions, lattice parameters, and cell volumes were fully relaxed with a plane-wave cutoff energy of 400 eV and a $1 \times 1 \times 1$ Monkhorst–Pack k-point meshes. The energy and force convergence criteria were set to 10^{-6} eV and 0.05 eV/Å, respectively.

3.2.3 Synthesis of MOFs

Synthesis of HKUST-1³³

NaOH (497 mg, 12.4 mmol) and trimesic acid (870 mg, 4.1 mmol) were added into a DI water (20 ml). A solution of $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1.5 g, 6.2 mmol) dissolved in EtOH (15 ml) was added in. Precipitate emerged immediately and the mixture was stirred briefly before the solid was separated via centrifugation. The solid was washed 3 times with EtOH before drying in a desiccator at room temperature overnight to give HKUST-1 as blue powder (~84% yield).

Synthesis of MIL-101 (Cr)³⁴

Benzene-1,4-dicarboxylic acid (332 mg, 2 mmol), $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (800 mg, 2 mmol) and HF, 48% in H_2O (40 μl , 2 mmol) were added into distilled water (9.6 ml) in a teflon-lined autoclave. The sealed mixture was heating in an oven at 200°C for 8 h. The resultant mixture was washed 3x with DMF and heated in EtOH (9 ml) at 80°C for 12 h. The heated mixture was then washed 3x with H_2O , 3x with EtOH, before drying in a desiccator overnight to give MIL-101 (Cr) as a green powder (~50% yield).

Synthesis of MIL-100 (Fe)³⁵

FeSO₄·7H₂O (3.41 g, 12.3 mmol) was dissolved in DI water (100 ml). A solution of NaOH (982 mg, 24.6 mmol) and trimesic acid (1.72 g, 8.2 mmol) in DI water (30 ml) was added in dropwise and the solution was stirred for 24 h. The resultant mixture was washed 3x with H₂O, 3x with EtOH and dried in an 80°C oven to give MIL-100 (Fe) as a brown powder (~73% yield).

Synthesis of UiO-66³⁶

ZrCl₄ (23.3 mg, 0.1 mmol), benzene-1,4-dicarboxylic acid (16.6 mg, 0.1 mmol) and acetic acid (1.37 ml) were dissolved in DMF (10 ml). The mixture was heated at 120°C for 24 h. The resultant slurry was washed 3x with DMF and 3x with MeOH before drying in 150°C vacuum oven to give UiO-66 as white powder (~77% yield).

3.2.4 Synthesis of MOF Composites

Synthesis of MOF/Fabric Composites

Cloth materials were cut into 4 × 4 cm pieces (~120 mg for cotton, ~150 mg for polyester and ~400 mg for nylon), soaked in EtOH and dried in oven before use. MOF powder (type and mass used as denoted in the name of the composite) and poly(acrylic acid) of equal mass were mixed in EtOH (400 μL) to form a MOF ink. The prepared MOF ink was dripped onto the fabric cloth and dried with N₂ gas to give the composite.

Synthesis of HKUST-1/Mask Composite

1 g of HKUST-1 and 1 g of PAA was dissolved in 10 ml of EtOH. The resultant suspension was coated onto a commercial respiratory dust mask, dried briefly with N₂ before desiccating at room temperature.

3.2.5 Anti-Bacterial Studies

Bacterial Culture

Escherichia coli and *Staphylococcus aureus* were incubated in Luria-Bertani (LB) medium at 37°C for 18 h with shaking. The concentration of bacteria was calculated by measuring the optical density at 600 nm (OD₆₀₀) using an UV-vis spectrometer. The bacteria suspension was then diluted to the appropriate level for further anti-bacterial experiments.

Anti-Bacterial Properties of Different Materials

200 µl of bacterial suspension (1×10^6 CFU mL⁻¹) was spread onto a LB plate. Different cottons samples of 1 cm x 1 cm (Blank Cotton, HKUST-1/Cotton-40mg, MIL-100(Fe)/Cotton-40mg, MIL-101(Cr)/Cotton-40mg, UiO-66/Cotton-40mg, PAA/Cotton-20mg) were pasted onto the LB plate before it was cultivated at 37°C for 18 h.

Anti-Bacterial Properties of HKUST-1/Cotton with Different Loading Amount

200 µl of bacterial suspension (1×10^6 CFU mL⁻¹) was spread onto a LB plate. Different cotton samples of 1 cm x 1 cm (HKUST-1/Cotton-xmg, x = 0, 5, 10, 20 and 40) were pasted onto the LB plate before it was cultivated at 37°C for 18 h. Inhibition distances were measured from the edge of the cloth to the nearest bacteria colony.

Time Related Anti-Bacterial Properties of HKUST-1/Cotton Composite

Three doses of bacterial suspension (1×10^8 CFU mL⁻¹) were sprayed onto 1 cm x 1 cm blank cotton and HKUST-1/Cotton-40mg respectively using a spray bottle. The bacteria on the cottons were collected by swabbing the cotton strips with wet cotton swabs at different time intervals (10/20/30 min) and submerging the contaminated swab in 200 µl of DI water. The solutions were diluted 1000 times and dripped onto LB plates for cultivation at 37°C for 18 h.

Anti-Bacterial properties of HKUST-1/Mask

Three doses of bacterial suspension (1×10^5 CFU mL⁻¹) were sprayed onto the surface of HKUST-1/Mask and blank mask respectively using a spray bottle. The bacteria on the masks were collected by swabbing the cotton strips with wet cotton swabs at different time intervals (10/20 min) and submerging the contaminated swab in 200 µl of DI water. 150 µl of the solutions were dripped onto LB plates for cultivation at 37°C for 18 h.

3.3 Result and Discussion

3.3.1 Initial Hypothesis and DFT Calculation

Figure 1. (a) Optimization of HKUST-1 structure for DFT calculation. (b) Coordination bonding between dimeric poly(acrylic acid) moiety with Cu atoms on HKUST-1 surface. (c) Electrostatic mapping showing electron distribution across the coordination bonds. (d) Adsorption energy for the interaction between glucose and HKUST-1 surface. (e) Adsorption energy for the interaction between glucose and loose carboxylic acid ends of PAA.

In order to achieve a practical and scalable methodology for the fabrication of MOF-fabric composites, a mean to coat raw MOF powder directly onto fabric substrates was developed. This method eliminates the long preparation time typically associated with in-situ growth of MOF onto substrates^{23, 26-27} and allows for more variety of MOFs to be coated, given that protocols for the preparation of MOF powders are more established. Binders are often used to improve the processibility of MOFs.³⁷⁻³⁸ As such, PAA was chosen for this purpose as it is a cheap and commercially available polymer used for textile processing.³⁹ Due to the abundance of carboxylic acid group present, we hypothesize that PAA will coordinate with valence metal sites on the surface of MOFs and effectively bind them to the fabric substrates to give functional composite materials. To establish control over the loading amount for MOFs, we planned to take advantage of the absorbing nature of fabrics and employed a drip cast methodology. The resultant product can be quickly dried under gas flow to vaporize the volatile solvent, leaving MOF and PAA securely attached onto the fabric substrate.

To verify our hypothesis, DFT simulation was conducted. HKUST-1 (Fig 1a) and a PAA moiety consisting of 2 repeating unit were chosen to model possible interactions between MOF surface and PAA substrate. The two oxygen atoms of the carboxyl group in PAA moiety form coordination bonds on HKUST-1 surface (Fig 1b). The bonding energy was calculated to be -2.086 eV, with 0.594 e^- gained by each oxygen atoms (Fig 1c). Based on our calculation, it is feasible for PAA to bind to the copper atoms on HKUST-1 surfaces to give PAA modified HKUST-1. In addition, the affinity between pristine HKUST-1/PAA modified HKUST-1 and fabric substrate was also determined. Glucose, a monomer of cellulose-derived cotton, was used to model fabric substrate and the absorption energy was calculated based on its interaction with either pristine HKUST-1 or PAA modified HKUST-1. The adsorption energy between glucose and PAA modified HKUST-1 is -0.798 eV (Fig 1e), which is significantly larger than that of between glucose and pristine HKUST-1 at -0.225eV (Fig 1d,). This indicates that surface modification with PAA enhances the affinity between HKUST-1 and fabric substrates, allowing for better adhesion during the formation of MOF-fabric composite.

3.3.2 Preparation of MOFs

4 different types of MOFs were prepared separately for the formulation of MOF-ink using established solution-based synthesis. The prepared MOFs exist in powder form, which were characterized extensively to ensure that they were crystalline and porous (Fig 2 and 3). All 4 MOFs chosen are archetypical MOF types containing different metal centres and organic linkers. They are easily identified by their distinct colours, which readily transferred onto materials they coated.

Figure 2. PXRD spectra and ATR-IR spectra of (a) MIL-101 (Cr), (b) HKUST-1, (c) UiO-66 and (d) MIL-100 (Fe)

Figure 3. N₂ isotherms and TGA spectra of (a) MIL-101 (Cr), (b) HKUST-1, (c) UiO-66 and (d) MIL-100 (Fe)

3.3.3 Preparation of MOF/Fabric Composites

Figure 4. (a) HKUST-1/Cotton-xmg samples, where $x = 5, 10, 20, 40$. SEM images showing gradual increase in the amount of HKUST-1 on fiber strands. (b) PXRD spectrum of HKUST-1/Cotton-xmg samples. As HKUST-1 loading increases, diffraction peaks corresponding to HKUST-1 become more well defined. (c) ATR-IR spectrum of HKUST-1/Cotton-xmg samples. Enhanced intensities at 1369 cm^{-1} (red region, -COO of HKUST-1) relative to that of around $900\text{--}1085\text{ cm}^{-1}$ (blue region, -CO of cotton) shows increasing amount of HKUST-1 loaded.

Figure 5. (a) HKUST-1/Cotton-40mg upon rolling, folding and cutting. (b) Visible dislodgement of HKUST-1 powder from cotton substrate with light abrasion, in the absence of PAA binder.

Preliminary study was conducted using HKUST-1. When poly(acrylic acid) (PAA) was mixed with HKUST-1, a suspension of MOF ink was formed. As predicted by the DFT calculation, HKUST-1/PAA ink can be easily dripped onto cotton fabric substrate. By premixing different amount of HKUST-1 and PAA, HKUST-1/Cotton-xmg ($x = 0, 5, 10, 20$ and 40) composites were obtained. Beyond HKUST-1/Cotton-40mg, the composite starts to lose its flexibility and visible dislodgment of the coated material can be observed. When PAA was not utilized, HKUST-1 powder also dislodged easily from the cotton fabric scaffold (Fig. 5b). The as-prepared materials exhibit an increasing shade of blue as loading increases, suggesting the successful incorporation of different amount of MOFs onto the cotton substrates (Fig. 4a). From the PXRD pattern, we see an increase in diffraction peaks intensities associated with HKUST-1 as MOF loading increases, which supports the initial visual observation for increasing MOF loading across the samples (Fig. 4b). Similarly, ATR-IR measurements show increasing intensity at 1369 cm^{-1} ($-\text{COO}$ of HKUST-1) relative to the $900\text{--}1085\text{ cm}^{-1}$ region ($-\text{CO}$ of cotton), further proving the precise control over the loading amount for the different samples (Fig. 4c). SEM images also show that the amount of MOF present on the surface of cotton fibers increases across the different samples (Fig. 4a). Thus, by using a drip cast method, the amount of MOF loaded onto fabric materials can be well controlled.

HKUST-1/Cotton-40mg was further investigated to shed more light into the resultant properties of the MOF-cotton fabric material. Weight difference between HKUST-1/Cotton-40mg and cotton suggest a high average loading efficiency of 85%, not accounting for mass transfer loss, showing that this is a very efficient loading method for the fabrication of MOF-based fiber composite. The resultant fabric retained physical properties of the fabric substrates, able to withstand rolling, bending, cutting etc., without any visible dislodgement of coated substance (Fig. 5a). Comparing the PXRD and ATR-IR spectra of HKUST-1/Cotton-40mg,

Figure 6. Material characterizations for HKUST-1/Cotton-40mg. (a) PXRD spectrum of composite compared to PAA coated cotton and pristine HKUST-1 powder. Inset showed a photo of the fabric composite. (b) N₂ isotherm comparing composite with PAA coated cotton. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine HKUST-1 powder. (d) TGA spectrum comparing composite with PAA coated cotton.

pristine HKUST-1 powder and cotton cloth coated with PAA revealed that the resultant composite possesses characteristic patterns of both its components (Fig. 6a and 6c). This suggest that the process does not significantly alter and compromise the structural integrity of HKUST-1 MOF. Well-defined HKUST-1 particles were observed by SEM on the coated HKUST-1/Cotton-40mg, with no observable morphological change as compared to the pristine HKUST-1 powder (Figure 7a and 7b). EDX scan of HKUST-1/Cotton-40mg also revealed the presence of Cu from HKUST-1, indicating the successful coating of the cotton substrate with

Figure 7. SEM images of (a) the composite and (b) HKUST-1. (c-d) EDX scan of Cu for the composite prepared.

MOF (Fig. 7c and 7d). N₂ adsorption/desorption studies (Fig 6b) showed that the composite's porosity slightly increase (BET surface area = 36 m²/g) over the PAA coated cotton substrate (BET surface area = 7 m²/g). Compared to the pristine HKUST-1 powder, a significant decrease in porosity was observed, possibly due to the weight contribution by the fabric substrate. Similar observation was seen from the TGA measurement, with no significant difference between HKUST-1/Cotton-40mg and PAA coated cotton substrate (Fig. 6d). By combining HKUST-1 with the cotton substrate, the resultant material retained the flexible property of the cloth while possessing additional functionalities induced by HKUST-1, giving a novel MOF-based fabric composite.

Figure 8. Material characterizations for HKUST-1/Polyester-50mg. (a) PXRD spectrum of composite compared to PAA coated polyester and pristine HKUST-1 powder. Inset showed a photo of the fabric composite. (b) N₂ isotherm comparing composite with PAA coated polyester. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine HKUST-1 powder. (d) TGA spectrum comparing composite with PAA coated polyester.

HKUST-1 was also coated onto other fabric materials, such as polyester and nylon. A similar protocol was utilized for the fabrication of HKUST-1/Polyester-50mg and HKUST-1/Nylon-135mg. Due to the weight differences for the different type of cloth, HKUST-1 and PAA added was adjusted accordingly to ensure that the theoretical wt% of loading remained constant. Similar to HKUST-1/Cotton-40mg, both polyester and nylon substrates were dyed blue after the coating, due to the HKUST-1 used. PXRD (Fig. 8a and 10a) and ATR-IR measurements (Fig. 8c and 10c) of the 2 samples showed similar observations as

Figure 9. SEM images of (a) the composite and (b) HKUST-1. (c-d) EDX scan of Cu for the composite prepared.

HKUST-1/Cotton-40mg, with characteristic patterns of the composites matching that of its respective components. SEM images also indicated that HKUST-1 particles were well coated onto the fibers, regardless of the type of fabric used (Fig. 9a, 9b, 11a and 11b). EDX measurements revealed the presence of Cu, from HKUST-1, on both polyester and nylon fiber strands (Fig. 9c, 9d, 11c and 11d). Unlike HKUST-1/Cotton-40mg, N₂ adsorption/desorption studies on the polyester and nylon composites revealed no significant gas uptake (Fig. 8b and 10b), further proving the initial hypothesis that the weight of the fabric used significantly affect the result obtained. TGA measurements further confirmed this observation (Fig. 8d and 10d). As such, it is reasonable to conclude that the applied strategy is not limited to cotton fabric, with the potential to be extended to other fabric materials as well.

Figure 10. Material characterizations for HKUST-1/Nylon-135mg. (a) PXRD spectrum of composite compared to PAA coated nylon and pristine HKUST-1 powder. Inset showed a photo of the fabric composite. (b) N₂ isotherm comparing composite with PAA coated nylon. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine HKUST-1 powder. (d) TGA spectrum comparing composite with PAA coated nylon.

This strategy was also demonstrated using other MOF types to further establish its generality. 3 other MOFs (MIL-100(Fe), MIL-101(Cr) and UiO-66) were chosen to expand the scope of this study. MIL-100(Fe)/Cotton-40mg, MIL-101(Cr)/Cotton-40mg, UiO-66/Cotton-40mg, were fabricated using a similar protocol as HKUST-1/Cotton-40mg. Like the HKUST-1 fabric, the other MOF fabrics adopted color from the MOF samples, suggesting the successful embedment of the various MOF materials onto the cotton substrates. PXRD (Fig. 12a, 14a, 16a) and ATR-IR measurements (Fig. 12c, 14c, 16c) of the various composites showed characteristic patterns of both MOFs and fabrics used, indicating that the various MOFs were added onto the fabric substrates. SEM images also showed that the various MOFs

Figure 11. SEM images of (a) the composite and (b) HKUST-1. (c-d) EDX scan of Cu for the composite prepared.

particles were well coated onto the fibers (Fig. 13a, 13b, 15a, 15b, 17a and 17b). EDX scan further supported this, with different metallic species from their parent MOFs detected on the fiber strands (Fig. 13c, 15c, 17c). N₂ adsorption/desorption studies revealed an observable difference in gas uptake for MIL-101(Cr)/Cotton-40mg as compared to the PAA coated cotton substrate (Fig. 16b), while negligible difference was observed for MIL-100(Fe)/Cotton-40mg and UiO-66/Cotton-40mg (Fig. 12b and 14b). This can be rationalized because pristine MIL-101(Cr) has significantly higher porosity compared to the other MOFs used, which compensated for the weight of the cotton fabric. However, TGA measurements revealed no significant difference for these samples (Fig. 12d, 14d and 16d). Nevertheless, it is clear that this strategy of producing MOF-fabric composites is applicable to various MOF types, proving that it is a general strategy adaptable to various fabrics and MOF types.

Figure 12. Material characterizations for MIL-100(Fe)/Cotton-40mg. (a) PXRD spectrum of composite compared to PAA coated cotton and pristine MIL-100(Fe) powder. Inset showed a photo of the fabric composite. (b) N₂ isotherm comparing composite with PAA coated cotton. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine MIL-100(Fe) powder. (d) TGA spectrum comparing composite with PAA coated cotton.

Figure 13. SEM images of (a) the composite and (b) MIL-100(Fe). (c) EDX scan of Fe for the composite prepared.

Figure 14. Material characterizations for UiO-66/Cotton-40mg. (a) PXRD spectrum of composite compared to PAA coated cotton and pristine UiO-66 powder. Inset showed a photo of the fabric composite. (b) N₂ isotherm comparing composite with PAA coated cotton. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine UiO-66 powder. (d) TGA spectrum comparing composite with PAA coated cotton.

Figure 15. SEM images of (a) the composite and (b) UiO-66. (c) EDX scan of Zr for the composite prepared.

Figure 16. Material characterizations for MIL-101(Cr)/Cotton-40mg. (a) PXRD spectrum of composite compared to PAA coated cotton and pristine MIL-101(Cr) powder. Inset showed a photo of the fabric composite. (b) N_2 isotherm comparing composite with PAA coated cotton. (c) ATR-IR spectrum of composite compared to PAA coated fabric and pristine MIL-101(Cr) powder. (d) TGA spectrum comparing composite with PAA coated cotton.

Figure 17. SEM images of (a) the composite and (b) MIL-101. (c) EDX scan of Cr for the composite prepared.

3.3.4 Anti-Bacterial Studies

Figure 18. Initial screening of various fabric substrate for (a) *Escherichia coli* (*E. Coli*) and (b) *Staphylococcus aureus* (*S. Aureus*) killing efficacies. (c) Bacteria killing efficacy of different samples with HKUST/Cotton-xmg, where x = 5, 10, 20, 40. (d) Inhibition distance measured for different HKUST/Cotton-xmg samples, where x = 5, 10, 20, 40.

Figure 19. (a) Bacteria killing efficacy of HKUST/Cotton-40mg across 10, 20 and 30min compared to pristine cotton fabric. (b) Survival rate of bacteria across different incubation periods on HKUST/Cotton-40mg.

To illustrate the functionalities of our MOF-fabric composites, we had decided to test them for their anti-bacterial properties. Cotton and PAA coated cotton samples were also prepared as controls. The various samples were incubated on LB plate coated with a layer of *Escherichia coli* (*E. Coli*). Preliminary result indicates that HKUST-1/Cotton-40mg is an excellent candidate for anti-bacterial study, as there is a clear and observable inhibition region without bacteria colony growth surrounding the composite material after the incubation period (Fig. 18a). Compared to the controls, it can be concluded that the antibacterial properties exhibited by HKUST-1/Cotton-40mg is a result of the HKUST-1 present, as neither the cotton nor the PAA coated cotton showed a similar result. Also, the MOF-fabric composites were further tested with a gram-positive bacterium, *Staphylococcus aureus* (*S. Aureus*), giving similar results (Fig. 18b). This shows that the antibacterial property of our MOF-fabric composite is general. Given the success of our initial screening attempts, HKUST-1/Cotton composite was selected for further study to quantify the antibacterial effect of the material. A detailed analysis using HKUST-1/Cotton-xmg ($x = 0, 5, 10, 20$ and 40) samples shows that the anti-bacterial properties of the composite material varied according to the amount of HKUST-1 loaded. Strips of HKUST-1/Cotton-xmg were incubated in LB plates with *E. Coli*. A gradual increase in the size of the rings surrounding HKUST-1/Cotton samples as HKUST-1 content increases further proves that HKUST-1 content in the composites is responsible for inhibiting bacteria growth (Fig. 18c and 18d). This agrees with literature findings, as a HKUST-1 variation $\text{Cu}_3(\text{NH}_2\text{BTC})_2$ MOF was shown to be effective against bacteria strains.²⁴ Also, several studies have established the antibacterial properties of HKUST-1.^{29, 40} We further tested the time-dependent killing efficiency of HKUST-1/Cotton-40mg by spraying a stock solution of *E. Coli* onto the materials directly before incubation. Samples were taken using cotton swabs at different time intervals to determine the amount of living bacteria present. This allows for a more realistic testing of our materials to gauge their performance under real-life scenario (eg.

Figure 20. (a) Photo of control mask without any coating. Bacteria present on control mask after 20min. (b) Photo of HKUST-1 coated mask. Bacteria present on HKUST-1 coated mask after 20min. (c) Morphology of bacteria incubated with blank cotton fabric. (d) Enlarged image of bacteria incubated with blank cotton fabric. (e) Morphology of bacteria incubated with HKUST/Cotton-40mg fabric. (f) Enlarged image of bacteria incubated with HKUST/Cotton-40mg fabric.

sneezing). As time elapsed, a gradual decrease in the number of bacteria colonies was observed (Fig. 19a and 19b). Most of the *E. Coli* sprayed onto the fabrics were killed and by 30 min, the *E. Coli* deposited were almost completely eradicated. This shows that our HKUST-1/Cotton sample is a very effective anti-bacterial material against contaminated bacterial droplets in air. To better understand the interactions between our prepared MOF/cotton fabrics and *E. Coli*, SEM were utilized for imaging. *E. Coli* incubated with HKUST-1/Cotton-40mg sample showed apoptosis of bacteria (Figure 20e and 20f) as compared to non-treated cotton cloth (Fig. 20c and 20d), further establishing the bacteria killing efficacy of our prepared composite material. This finding has huge implications for future medical and healthcare applications, as this methodology can be utilized to fabricate protective wearables for frontline healthcare workers.

To further show that the coating strategy is effective for the fabrication of protective wearables, we coated a commercial mask with the same solution containing HKUST-1 and PAA to give a HKUST-1/mask composite (Fig. 20b). Similarly, stock solution of bacteria was

sprayed onto the coated mask to simulate contaminated droplets in air. Compared to the control (Fig. 20a), bacteria growth was inhibited due to the presence of HKUST-1 on the mask composite, granting it anti-bacterial properties. A distinct difference can be observed after 20 minutes of incubation, for the HKUST-1 coated mask showing high bacteria killing efficacy (Fig. 20a and 20b). Once again, our method was shown to be versatile, not solely limited to the production of functional cloth fabrics. This methodology can be utilized for the commercial manufacturing of useful antibacterial wearables in general, which is essential to help healthcare professionals in times of crisis.

3.4 Conclusion

In this project, we have introduced a practical strategy to coat MOFs onto fabric materials using PAA as the binder. The method was demonstrated to be fast and simple for the downstream processing of powdered MOF precursors into usable products. Not only can this method control the amount of MOF loaded onto fabrics, but it can also be applied to coat a wide variety of MOF securely onto different fabric substrates. The resultant composite materials retained the flexibility imparted by the fabric while possessing unique properties due to the MOF embedded. One of the composite prepared, HKUST-1/Cotton, was demonstrated to have strong anti-bacterial properties, due to the MOF present. This versatile method can be readily scaled up for the commercial production of MOF-coated products, such as protective wearables for healthcare workers, due to its simple and efficient coating process. We envision that this unprecedented methodology will revolutionize the industrial processing of MOFs in combination with fabric materials, to give useful and functional MOF-based composites in the future.

3.5 References

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Chapter 4

ZIF-8 Nanoparticles for Facile Processing into Useful Fabric Composite

4.1 Introduction

In chapter 2 and 3, we have seen the importance of developing new scalable synthetic methodology to produce MOFs, as well as new strategies to effectively process powdered MOFs substrates into usable materials. In this chapter, we will combine these 2 separate directions to see how they sequentially contribute towards the realization of MOF commercialization.

ZIF-8, one of the earliest zeolitic imidazolate framework discovered in 2006, was constructed with pore diameter of 12.5 Å and pore aperture of 3.3 Å.¹ This archetypical MOF displays exceptional water and chemical stability, largely attributed to its strong Zn-N coordination bonding.² Combined with the possibility of post synthetic modification (PSM), such as linker exchange,³ and easy processing into composite materials,⁴ it is no doubt that ZIF-8 holds tremendous potential as a promising solution for a wide range of problems. But like other MOFs, the lack of suitable scalable synthetic methodology to produce large quantity of ZIF-8 nanocrystals⁵ and difficulty in processing ZIF-8 from the powdered form to functional composites,⁶⁻⁸ impeded the usability for practical applications. Harsh solvothermal conditions over a long period of time for crystallization are typical synthetic conditions for the synthesis of ZIF-8.^{1, 9-10} Furthermore, the yield resulting from such synthesis are often less than ideal and the quality of crystals formed upon scaling up pales in comparison to that of small-scale production. Also, there is a lack of practical solutions to produce ZIF-8 composites. Many existing composites relies on in-situ formation of ZIF-8 onto substrates to give composite materials.¹¹⁻¹² This is not feasible for the production of materials in industry as it is time consuming and not cost-efficient. Therefore, it is necessary to explore an effective pathway for

the development of MOF-based composites products to realize their potential in addressing real-world problems.

To address these 2 key issues surrounding MOFs commercialization, we have developed an industrially relevant process to produce functional ZIF-8 coated fabric composite, via an improved synthetic methodology for scalable production of ZIF-8 powder and a facile drip-cast mean to introduce ZIF-8 onto cotton substrate. Using a base-assisted deprotonation strategy, we are able to produce gram scale quantity of pristine ZIF-8 instantaneously with a high yield. The prepared ZIF-8 powder was mixed with polystyrene solution and easily drip-casted onto cotton textile to give ZIF-8/cotton composite materials. The entire process uses green solvents and is carried out at room temperature, using commercially available chemicals and materials. The resultant composite showed significant enhancement in dye absorption for methyl orange (MO) and rhodamine B (RB), due to the presence of ZIF-8 embedded. Also, the composite exhibits antibacterial properties for both gram-positive and gram-negative *Staphylococcus aureus* (*S. aureus*) and *Escherichia coli* (*E. coli*) respectively, which is promising for the development of new MOF-based material for healthcare applications. This work highlights the significance of an elegant and practical solution for MOF commercialization, which has huge relevance for the industrial production of functional MOF and MOF-based composite products.

Scheme 1. Facile pathway to obtain ZIF-8/Fabric composite.

4.2 Experimental Section

4.2.1 Materials and Characterizations

All reagents and solvents are commercially available and used without further purification. 2-Methylimidazole (99%), zinc nitrate hexahydrate (98%) and polystyrene (Mw ~ 192000) were purchased from Sigma-Aldrich. Zinc nitrate hexahydrate (>99%) and NaOH (>99%) were obtained from Sinopharm Chemical and Reagent Co. Tech grade ethanol, ethyl acetate and deionized water were used as solvents. Powdered x-ray diffraction (PXRD, Cu-K α radiation, 40 kV, 15 mA) were carried out at room temperature over a 2θ range of $5^\circ - 50^\circ$, using a Rigaku MiniFlex 600 benchtop diffractometer. Baselines were zeroed using JADE5 software. Thermogravimetric analysis (TGA) was conducted by heating the weighted sample at $10^\circ\text{C}/\text{min}$ under N₂ flow (60mL/min) from 30°C to 800°C , using a TGA-Q500 Thermoanalyzer. N₂ adsorption/desorption studies were carried out using Quantachrome Autosorb-iQ with pure N₂ gas. Brunauer-Emmet-Teller (BET) surface areas were calculated by predetermined adsorption points measured, using the micropore BET assistant function in the Quantachrome ASiQwin software. Fourier transform infrared (FTIR) spectra were recorded in attenuated total reflectance (ATR) mode using a Perkin-Elmer 100 FTIR spectrometer. Scanning electron microscopy (SEM) images were taken with a JEOL JSM-7600 field emission scanning electron microscope operating at 5.0 kV. Energy-dispersive x-ray spectroscopy (EDX) was carried out using the same equipment at 15.0 kV. Contact angles experiments were conducted by dripping a 4 μL ultrapure water droplet onto the samples, recorded using a Theta Lite tensiometer equipped with a Firewire digital camera. UV-vis spectroscopy was carried out using a Shimadzu UV-3600 UV-Vis-NIR spectrophotometer over a range of 200-900 nm.

4.2.2 Synthesis of MOF and Composite Materials

ZIF-8-(C)¹³

Synthetic protocol was adapted from literature report. $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (1.17 g, 3.93 mmol) dissolved in 8 ml of DI H_2O was added to a solution containing 2-methylimidazole (22.70 g, 276.50 mmol) in 80 ml of DI H_2O . The solution was stirred for approximately 5 min before the product was isolated via centrifugation. The crude product was washed with DI H_2O and EtOH, dried in 65°C oven to give ZIF-8-(C) as a white crystalline powder (0.828 g, 92.5% by Zn salt used).

ZIF-8-(S)

NaOH (73.2 mg, 1.83 mmol) and 2-methylimidazole (136.6 mg, 1.66 mmol) was added into 4 ml of DI H_2O . $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (247.5 mg, 0.83 mmol) dissolved in 4 ml of EtOH was poured into the first solution to induce precipitation of ZIF-8. The resultant solution was briefly mixed with a vortex stirrer before centrifugation. The crude product was washed with DI H_2O and EtOH, dried under vacuum at room temperature overnight to give ZIF-8-(S) as a white crystalline powder (161.5 mg, 85.3%).

ZIF-8-(L)

NaOH (6.26 g, 157 mmol) and 2-methylimidazole (11.69 g, 142 mmol) was added into 150 ml of DI H_2O . $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (21.18 g, 71 mmol) dissolved in 150 ml of EtOH was poured into the first solution to induce precipitation of ZIF-8. The resultant solution was briefly stirred before centrifugation. The crude product was washed with DI H_2O and EtOH, dried in 65°C oven overnight to give ZIF-8-(S) as a white crystalline powder (15.4 g, 95.1%).

PS/Cotton

The procedure was modified from similar protocol used in chapter 3. Cotton cloth was cut into 4 x 4 cm pieces (~120 mg), soaked in EtOH and dried in an oven. 400 μ l of polystyrene in ethyl acetate stock solution (100 mg/ml) was diluted with 1ml of ethyl acetate and drip coated over the prepared cotton fabric. The volatile solvent was easily evaporated over Ar gas to give the composite sample.

ZIF-8/Cotton-40mg

The procedure was modified from similar protocol used in chapter 3. Cotton cloth was cut into 4 x 4 cm pieces (~120 mg), soaked in EtOH and dried in an oven. 400 μ l of polystyrene in ethyl acetate stock solution (100 mg/ml) was diluted with 1ml of ethyl acetate. 40 mg of ZIF-8-(L) was dispersed in the resultant solution and sonicated. The suspension was drip coated over the prepared cotton fabric. The volatile solvent was easily evaporated over Ar gas to give the composite sample.

4.2.3 Density Functional Theory (DFT) Calculation

All calculations were conducted on the Vienna ab initio simulation package (VASP 5.4.4) and the exchange and correlation functional were treated as generalized gradient approximation (GGA) of the Perdew–Burke–Ernzerhof (PBE) formula. The styrene dimer was utilized to model polystyrene, while glucose was used to model cotton fiber. The (100) facet of ZIF-8 was utilized as the MOF substrate for simulation. The periodic ZIF-8 structure, ZIF-8-PS, ZIF-8-PS-Fiber were optimized and its ionic positions, lattice parameters, and cell volumes were fully relaxed with a plane-wave cutoff energy of 400 eV and a $1 \times 1 \times 1$ Monkhorst–Pack k-point meshes. The energy and force convergence criteria were set to 10^{-5} eV and 0.02 eV/Å, respectively. The adsorption energy E_{ad} was defined by the following equation:

$$E_{ad} = E_{total} - E_{slab} - E_{molecule}$$

where E_{total} is the total energy of a molecule adsorbed on ZIF-8 surfaces; E_{slab} is the energy of the ZIF-8 surface; $E_{molecule}$ is the energy of the adsorbed molecules.

4.2.4 Dye Absorption Experiments

Methyl orange (65.5 mg, 0.2 mmol) was dissolved in 200 ml of DI water to give a 10^{-3} M stock solution. Calibration curve was constructed from 2.5×10^{-6} M to 5.0×10^{-5} M using diluted samples from the stock solution. Rhodamine B (19.2 mg, 0.04 mmol) was dissolved in 400 ml of DI water to give a 10^{-4} M stock solution. Calibration curve was constructed from 1.0×10^{-7} M to 5.0×10^{-6} M using diluted samples from the stock solution. 1 ml of methyl orange (5.0×10^{-5} M) / rhodamine B (5.0×10^{-6} M) were used initially for the filtration experiments. 3 pieces of circular membranes (~1.3cm diameter) were cut out from PS/cotton or ZIF-8/cotton-40mg composites to fit into a milipore swinnex membrane filter. The 1ml solution was passed through the filter membranes thrice via syringe filtration (1 cycle) before the corresponding UV-vis spectrum was recorded. This process was repeated 5 more times to obtain measurements for 6 cycles of filtration. The same experiment was repeated 2 more times to obtain standard deviation and average.

4.2.5 Anti-Bacterial Studies

Bacterial Culture

Escherichia coli (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) were cultivated in Luria-Bertani (LB) medium at 37°C for 18 h with constant shaking. The concentration of bacteria was calculated by measuring the optical density at 600 nm (OD600) using a UV-vis spectrometer. Bacteria were diluted to appropriate concentrations to conduct further anti-bacterial experiments.

Anti-Bacterial Properties of Different Fabric Samples

150 μL of the bacterial suspension (1×10^4 CFU mL^{-1}) was spread on a LB plate. Different fabric samples (cotton, PS/cotton and ZIF-8/cotton-40mg, approximately 1cm x 1cm) were pasted onto the plate and cultivated at 37°C for 18 h.

Time Dependent Anti-Bacterial Properties of ZIF-8/Cotton Composite

ZIF-8/cotton-40mg (approximately 1cm x 1cm) was soaked and stirred in 1 mL of bacterial suspension (1×10^4 CFU mL^{-1}) for different amount of time (0/10/20/30 min). After which, 150 μL of the bacterial suspension was drawn and spread on LB plate for cultivation at 37°C for 18 h.

4.3 Result and Discussion

4.3.1 Rapid Synthesis of ZIF-8

Long reaction time, typically associated with the crystallization process, greatly impeded the large-scale production of MOFs. In recent years, base-assisted synthesis has shown to significantly reduce the time taken for MOF formation by promoting coordination bonding.¹⁴⁻¹⁶ For ZIF-8, the addition of a base to the 2 precursors, 2-methylimidazole (2mim) and zinc salt (Zn), can accelerate the crystallization of ZIF-8.⁵ Early research utilized a large excess of 2-methylimidazole (2mim:Zn $\approx$ 70) as base during the formation of ZIF-8.¹³ Quality ZIF-8 nanocrystals were obtained by this methodology, at the expense of linker wastage. To address this problem, Wang et. al. reported an improved ZIF-8 synthetic methodology using a mixture of polymer surfactant and NH₄OH additives to keep precursors at stoichiometric ratio (2mim:Zn = 2).¹⁷⁻¹⁸ However, the additives used were also in large excess compared to the ZIF-8 precursors, which was not ideal as well due to the cost associated with waste solvent treatment. To improve upon existing synthetic protocols, we intend to use a strong base (i.e., NaOH) for the synthesis of ZIF-8 products. 2mim would be deprotonated completely to hasten the coordination bonding with the Zn source to achieve rapid crystallization. This strategy could limit the amount of base added and also keep the stoichiometric ratio of 2mim:Zn at 2 during the ZIF-8 synthesis.

A small-scale synthesis was carried out to test our hypothesis. A slight excess of NaOH (NaOH: 2mim = 1.1) was utilized to ensure the complete deprotonation of the 2mim precursors in water, before combining it with a solution of ethanolic Zn(NO₃)₂. White precipitation was observed instantaneously upon mixing, which can be easily separated and washed to obtain ZIF-8-(S), with a high isolated yield of 85.3%. Various characterizations were carried out to study the properties of ZIF-8-(S) prepared. ZIF-8-(C) sample, obtained via a conventional

Figure 1. (a) PXRD patterns of ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L) synthesized. (b) N₂ isotherms measured for ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L). (c) ATR-IR spectra of ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L) synthesized. (d) TGA recorded for ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L).

protocol,¹³ was also synthesized for comparison. PXRD pattern of the newly prepared ZIF-8-(S) matches with that of ZIF-8-(C), suggesting that ZIF-8 was successfully synthesized following the new protocol (Fig. 1a). This was confirmed by the matching ATR-IR spectra (Fig. 1c). SEM image shows that ZIF-8-(S) synthesized were more irregularly shaped and sized compared to ZIF-8-(C) (Fig. 2b). This is likely due to the fast rate of precipitation during the formation of ZIF-8-(S), which impeded morphological control. Type 1 N₂ isotherm was recorded for ZIF-8-(S), similar to that of ZIF-8-(C) (Fig. 1b). Although the calculated BET surface area of ZIF-8-(S) (1051 m²/g) is lower than that of ZIF-8-(C) (1534 m²/g), it is still comparable to other ZIF-8 samples reported in the literature.¹⁸⁻¹⁹ Similar to ZIF-8-(C), ZIF-8-

Figure 2. (a) Large scale synthesis of ZIF-8-(L) in 500ml bottle. (b) SEM images of ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L) prepared.

(S) has high thermal stability, as measured by TGA (Fig. 1d). As such, by using NaOH-assisted deprotonation strategy, ZIF-8 can be produced very efficiently.

Encouraged by this result, a scaled-up synthesis was carried out. 15.4 g of ZIF-8-(L) sample was isolated easily following the modified synthetic protocol, with a near quantitative yield of 95.1% (Fig. 2a). PXRD and ATR-IR spectra were both similar to ZIF-8-(C) and ZIF-8-(S), suggesting that ZIF-8-(L) synthesized were of excellent quality (Fig. 1a and 1b). SEM images of ZIF-8-(S) and ZIF-8-(L) were also similar to each other, indicating that the scaling up process does not significantly affect the morphology of ZIF-8 nanoparticles produced (Fig. 2b). N₂ adsorption/desorption properties of ZIF-8-(L) was also much better than both ZIF-8-(C) and ZIF-8-(S), with a calculated BET surface area of 1552 m²/g (Fig. 1b). TGA profile of

ZIF-8-(L) was also similar to ZIF-8-(C) and ZIF-8-(S), revealed that the scaled-up sample has high thermal stability (Fig. 1d).

Although there are slight differences observed between ZIF-8-(C), ZIF-8-(S) and ZIF-8-(L) samples, it is reasonable to conclude that the ZIF-8 samples prepared by this rapid, scalable precipitation method were of excellent quality. This protocol eliminated the use of heat to induce crystallization and significantly reduced excess reagents used. In addition, only green solvents (i.e., EtOH and DI water) were utilized to give ZIF-8 products in high yield. Thus, this synthetic methodology has a huge potential to be developed for industrial use.

4.3.2 Preparation of ZIF-8/Cotton Fabric using Polystyrene Binder

While the large-scale synthesis of ZIF-8 is essential for its commercialization, the subsequent processing into usable MOF-based product is equally important as well. MOFs in their powdered form posed several problems, such as inhalation risk and clogging, which impeded their use in practical applications. One of the most promising and versatile method is to develop it into a coating to be applied onto surfaces. In chapter 3, we have described a post-synthetic modification strategy using poly(acrylic acid) to coat powdered MOFs onto fabric substrates. While this is largely successful for carboxylic acid-based MOFs (i.e., HKUST-1, MIL-101 (Cr), MIL-100 (Fe) and UiO-66), the same method cannot be applied to azolate-based MOF such as ZIF-8. Unlike most MOFs, ZIF-8 surface is terminated with 2mim ligands, instead of uncoordinated metallic secondary building units.²⁰ In order to address this problem, we proposed the use of an alternative binder, polystyrene (PS). Styrene moieties can potentially form π - π interactions with 2mim on the surface of ZIF-8 nanoparticles for effective binding. We hypothesize that this strategy would be more favorable to bind ZIF-8 onto cotton substrate to give the desirable ZIF-8/cotton composite product.

Figure 3. a) Optimization of ZIF-8. b) Electrostatic charge separation between dibenzene moiety and 2-methylimidazole on ZIF-8. c) Adsorption energy between dibenzene moiety and 100 facet of ZIF-8. d) Adsorption energy between dibenzene moiety and glucose molecule.

To test our hypothesis, molecular simulation was done to check the feasibility of this method (Fig. 3a). Dibenzene moiety and glucose molecule were chosen to model the PS component and cotton substrate respectively. Binding energy between dibenzene and the 100 facet of ZIF-8 was calculated to be -0.21 eV, with a charge separation of 1.88 e^- across the 2 components (Fig 3b and 3c). The binding energy between glucose and dibenzene is also thermodynamically feasible at -0.1eV (Fig 3d). This shows that it is theoretically possible to use PS as a binder for the fabrication of ZIF-8/cotton composite material.

As predicted by the molecular simulation, a MOF-polymer suspension can be obtained by mixing PS with ZIF-8-(L) in ethyl acetate (EA). The resultant mixture can be easily drip-

Figure 4. (a) PXRD pattern of ZIF-8-(L), PS/cotton and ZIF-8/cotton-40mg composite. Inset shows a photo of ZIF-8/cotton-40mg prepared. (b) N_2 isotherms of ZIF-8/cotton-40mg compared to PS cotton sample. (c) ATR-IR measurements of ZIF-8-(L), PS/cotton and ZIF-8/cotton-40mg composite. (d) TGA of ZIF-8/cotton-40mg compared to PS cotton sample.

coated onto cotton fabric substrate to obtain a ZIF-8 coated cotton composite. The PS binder prevents dislodgement of ZIF-8 powder when ZIF-8/cotton-40mg was subjected to physical stress, such as folding, bending and cutting, to give a robust fabric composite. A high average loading efficiency of 80.7% was achieved, as determined by the increase in weight measured. This does not account for mass transfer loss, which suggest that it is a very efficient mean to load MOF onto cotton fabric substrate. The preparation process does not require any sophisticated equipment and can be readily translated to existing textile manufacturing process, such as spray coating.

Figure 5. (a) SEM images of PS/cotton (top) and ZIF-8/cotton-40mg (bottom). (b) EDX mapping of C, N and Zn for ZIF-8/cotton-40mg.

Figure 6. Contact angle measurements of cotton, PS/cotton and ZIF-8/cotton-40mg.

ZIF-8/cotton-40mg was subjected to various characterization techniques to further study its properties. PXRD of the composite material contained spectrum lines corresponding to both ZIF-8(L) and PS coated cotton substrate, suggesting the successful incorporation of ZIF-8 onto the fabric material (Fig. 4a). This is further supported by the result from ATR-IR measurements (Fig. 4c). SEM images showed that the cotton fibers were coated with a thin layer of granular substrate, consistent with the shape and size of ZIF-8 particles synthesized (Fig 5a). To further confirm the identity of the coated substrate, EDX was conducted to detect the elemental compositions of the resultant fabric material. The presence of nitrogen and zinc on the fiber strands further proved that the coated substance contains ZIF-8 nanoparticles, since the 2 elements were absent from pristine cotton fabric and PS binder (Fig. 5b). N₂

absorption/desorption isotherm of ZIF-8/cotton-40mg significantly differs from that of PS/cotton control, due to the porous nature of ZIF-8 on the composite material (Fig. 4b). There is a significant BET surface area measured for ZIF-8/cotton-40mg composite ($166 \text{ m}^2/\text{g}$) as compared to PS/cotton ($7 \text{ m}^2/\text{g}$). However, TGA measurements were not very different for the 2 samples (Fig. 4d). Nevertheless, it is reasonable to conclude that ZIF-8 was successfully coated onto the cotton substrate to give a novel composite material. Contact angles with water were also measured to determine the surface properties of the resultant composite material (Fig. 6). Due to the hydrophobic nature of PS, PS/cotton sample is also hydrophobic, with a contact angle of 109.5° . Similarly, ZIF-8/cotton-40mg is also hydrophobic, with a slightly higher contact angle of 113.5° .

4.3.3 Dye Absorption Capability of ZIF-8/Cotton Fabric

Figure 7. UV-vis spectra of methyl orange (MO) filtration with (a) PS/cotton and (b) ZIF-8/cotton-40mg as filter membrane; Rhodamine B (RB) filtration with (d) PS/cotton and (e) ZIF-8/cotton-40mg as filter membrane. Insets show solution and filter membrane after 6 cycles of filtration. (c) MO and (f) RB absorption capabilities of PS/cotton and ZIF-8/cotton-40mg summarized.

Given the water-resistant nature of the prepared composite product, we tested ZIF-8/cotton-40mg for its ability to remove organic dyes from aqueous solution.²¹⁻²² 2mm terminated surfaces of ZIF-8 are electrostatically charged in aqueous solution, due to the protonation/deprotonation of aromatic nitrogen present, which enhances its dye absorption capability. Circular filter membranes were cut from the as-prepared composite to fit into a syringe membrane filter. Cationic RB and anionic MO were selected to test the dye absorption capability of ZIF-8/cotton-40mg prepared, and comparisons were made with PS/cotton control. Significant decolorization of the dye solution was observed after 6 cycles of MO filtration, as compared to the control. At the same time, ZIF-8/cotton-40mg filter membrane was dyed yellow relative to the control membrane. This was also reflected by the UV-vis spectroscopic transmittance measurements at 464nm for the 2 samples. No observable absorption was recorded for PS/cotton membrane while a gradual decrease in the peak measured at 464nm was detected for ZIF-8/cotton-40mg membrane (Fig. 7a and 7b). 77% of MO was absorbed by ZIF-8/cotton-40mg after 6 cycles of filtration, as opposed to negligible absorption for PS/cotton (Fig. 7c). Similarly, decolorization of RB solution and dyeing of ZIF-8/cotton-40mg membrane was observed after 6 cycles of filtration. Rapid absorption of RB, as seen from the decrease in UV-vis transmittance at 555 nm, for ZIF-8/cotton-40mg membrane was observed after 6 filtration cycles, in contrast to the marginal decrease in intensity when PS/cotton membrane was used (Fig. 7d and 7e). 90.6% of RB was absorbed by ZIF-8/cotton-40mg after 6 cycles of filtration, while only 13.9% was recorded when PS/cotton was used (Fig. 7f). The increase in absorption capacity was attributed to the presence of ZIF-8 on the composite membrane. It is clear that ZIF-8 nanoparticles still retained their absorption capacity even after they were mixed with PS and coated onto the cotton substrate. The ZIF-8 coating endows pristine cotton fabric with unique properties of the MOF, allowing for its use in practical applications, such as dye removal by filtration.

4.3.4 Anti-Bacterial Studies

Figure 8. (a) Initial screening of antibacterial properties using *Escherichia coli* (*E. coli*) and *Staphylococcus aureus* (*S. aureus*) with cotton (top), PS/cotton (bottom right) and ZIF-8/cotton-40mg (bottom left). (b) SEM images of *S. aureus* incubated with cotton control and ZIF-8/cotton-40mg. (c) Time-dependent incubation test for bacteria killing efficacy.

The prepared ZIF-8/cotton-40mg was further tested for its antibacterial properties. Initial screening was done by placing cotton, PS/cotton and ZIF-8/cotton-40mg substrates onto an agar plate containing gram-negative *Escherichia coli* (*E. coli*). After incubation for 18 h, bacteria growth was inhibited by the ZIF-8/cotton-40mg sample solely, clearly demonstrating the antibacterial properties exhibited by ZIF-8 nanoparticles (Figure 8a). The same experiment was repeated using gram-positive *Staphylococcus aureus* (*S. Aureus*) and the result was even more prominent, with a larger region of inhibition (Figure 8a). Several notable studies have also shown that ZIF-8 is a promising material for anti-bacterial applications.²³⁻²⁵ The mechanism behind bacteria killing of ZIF-8 nanoparticles is not known, but it is widely proposed that the release of antibacterial MOF components is responsible for the bacteria

killing efficacy.²⁶ Zinc ions and imidazole derivatives were both shown to effectively inhibit microbial growth.²⁷⁻²⁸ The significant enhancement in bacteria inhibition for gram-positive *S. aureus* in relation to gram-negative *E. coli* could be due to the higher free fatty acid content present in the former strain, which 2-methylimidazole specifically targets.²³ To investigate this antibacterial phenomenon further, SEM images of *S. aureus* sample incubated with cotton control and ZIF-8/cotton-40mg were taken (Figure 8b). Compared to the cotton incubated sample, *S. aureus* incubated with ZIF-8/cotton-40mg sample exhibits significant morphological change. The surface of the bacteria appears to be wrinkled and transmembrane lysis tunnels were observed, suggesting that the cell membrane was severely disrupted, leading to cell death. This can be attributed to the presence of ZIF-8 in ZIF-8/cotton-40mg composite. To quantify the bacteria killing efficacy of ZIF-8/cotton-40mg composites, ZIF-8/cotton-40mg composite was incubated with *S. aureus* for different intervals of time (Figure 8). Significant decrease in the number of bacteria colonies present was observed with increasing incubation time. Within 30 minutes of incubation, less than 0.5% of bacteria remains. This shows that ZIF-8/cotton-40mg composite is very effective in killing gram-positive bacteria strain, such as *S. aureus*. The antibacterial ZIF-8/cotton-40mg composite fabric would be useful as the global demand for quality healthcare products increases, in light of the recent corona virus disease (COVID-19) pandemic.

4.4 Conclusion

In this work, we have successfully developed a feasible pathway to fabricate ZIF-8/cotton composite from commercially available components. The entire facile synthesis and fabrication step proceeds rapidly, using only green solvents (i.e., water, EtOH, EA), without heating and extensive wastage of reactants. Large scale production of ZIF-8 can be easily achieved and can be further optimized to be adapted for industrial production. The prepared MOF was obtained in high yield and is comparable to samples prepared using other synthetic means. It can be further processed into a suspension by mixing with commercially available PS binder, to be drip-casted onto cotton textile fabric. The prepared composite material, ZIF-8/cotton-40mg, was robust and flexible, with good water-resistant properties. Also, it showed significant enhancement in the absorption of organic dye RB and MO, as well as superior bacteria killing efficacy, due to the presence of ZIF-8 embedded. This protocol considered the practical needs of MOF commercialization and is designed specifically for the transition to industrial production. This work has the potential to inspire future developments for large-scale production of MOF and their subsequent processing into usable materials.

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Chapter 5

Conclusion and Future Work

5.1 Summary and Outlook

In this thesis, we have looked at several synthetic methodologies which have the potential to be developed into synthetic protocol for large-scale production of MOF materials. By utilizing dry heating strategy in chapter 2, solvent and corrosive HF modulator can be eliminated from the synthetic procedure for MIL-88B (Cr) and MIL-53 (Cr) MOFs. In chapter 4, base-assisted synthesis with NaOH promote the rapid formation of ZIF-8 nanoparticles at room temperature. The procedure utilized green solvents and the products were isolated in high yield. Minimal waste was produced, and the strategy was shown to be scalable. We have also developed a useful and facile strategy to incorporate of MOF onto fabric surfaces using polymer binders in chapter 3 and 4. Supramolecular interactions between MOFs and polymer binders give rise to MOF-polymer coatings, which can be easily applied to surfaces. This strategy can be used in the production of MOF-fabric composites, which have the potential to be developed into protective wearables for healthcare applications. This thesis has shown the importance of developing industrially relevant MOF production and processing methodologies, towards the goal of MOF commercialization.

Subsequent developments of the ideas put forth in this thesis are necessary to realize the end objective of translating research from academia to industry. In chapter 2, the mechanism behind the selective formation of MIL-88B (Cr)/MIL-53 (Cr) should be elucidated to understand the MOF formation process from a theoretical perspective. Also, the reaction could be scaled up further and optimized to check if it is still feasible and relevant for industrial production. Exploration of potential application, especially for MIL-88B (Cr), should be carried out as well. In chapter 3, MOF-fabric composites prepared could be more thoroughly

evaluated for their physical properties, such as tensile strength and stability, to give a more comprehensive evaluation on how these materials fare in practical usage. Large scale coating methods based on drip-casting could also be developed and adapted for continuous fabric coating. Similarly, in chapter 4, scaling up of synthesis and processing techniques are important aspects for practical considerations in the fabrication of ZIF-8 based composite materials.

Although these studies are significant in contributing to the development of MOF for commercial use, they are by no means comprehensive in the larger scheme of things. There are still plenty of rooms for improvement as the demand for MOF products increases. With industries gradually recognizing MOF potential as a viable solution to many real-world problems, mass production of MOFs for commercial use is being realized through the efforts from industrial giants (e.g. BASF, Strem, etc.) and chemical start-ups (e.g. MOF Technology, NuMat, NovoMOF, etc.). The cost of MOFs is expected to decrease as production means improve, making MOF products more competitive compared to other similar materials. Most commercially available MOF products are currently limited to archetypical MOFs. This is due to the commercial availability of organic linkers, which makes the production of the resultant MOF products cost-efficient. At the same time, archetypical MOFs have better stability and are more well understood.¹ As such, it would be worthwhile to explore the large-scale production of other promising MOF types, such as Zr-based MOFs or metal azolate frameworks, which are also well known for their high chemical stability.²⁻³ Most MOFs synthesized are unstable in water or even moist air, due to the hydrolysis of coordination bonds, which greatly hinder the desire to industrialize MOFs.¹ To address this issue, several methods were reported based on post-synthetic processes.⁴⁻⁶ While these processes are not yet demonstrated on a large scale, they open up new possibilities for less stable MOF types to be commercialized. Alternatively, MOFs can also be utilized for the preparation of other functional carbon materials, which possess better stability than pristine MOFs.⁷⁻⁹ This

conversion is mainly achieved by the pyrolysis of framework materials under controlled conditions, which is an established industrial process to obtain porous carbon materials such as activated carbon/charcoal. Besides MOF production, it is also a huge challenge for the downstream processing of MOFs to fabricate functional MOFs products practically. Although some facile and effective strategies are available for the fabrication of MOF-based products, product development still has a long way to realize the full potential of MOF-based materials for real-world applications, as very few studies demonstrated large scale processing of MOF composite materials in bulk. Some methods, such as wash-coating of MOFs onto solid support, are not well explored for MOF processing as well. Also, there are several other material fabrication methodologies that bypass the MOF powder intermediates (e.g., seed-and-grow methods,¹⁰⁻¹¹ heat pressed imprint,¹²⁻¹³ and vapor deposition techniques¹⁴⁻¹⁵), which are not described within the scope of this thesis despite their relevance to large-scale production of functional MOF materials. As such, new and exciting developments are expected in the near future for this emerging field of study.

By evaluating both the MOF production and material development process, this thesis has provided a unique perspective on the development of MOF. While it is essential to continue pushing for new frontiers in MOF applications, it is equally important to develop technologies to translate MOF materials from laboratory to industrial scale in order to realize their applications. As we are only at the early stage of exploring the commercialization of MOF products, it is important for experts from different fields and specializations to work closely together in order to make MOF commercialization into a reality.

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