Synthesis and self-assembly of metal-organic frameworks

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**NANYANG
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**SYNTHESIS AND SELF-ASSEMBLY OF METAL-
ORGANIC FRAMEWORKS**

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SYNTHESIS AND SELF-ASSEMBLY OF METAL-ORGANIC FRAMEWORKS

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Abstract

Metal-organic frameworks (MOFs), also known as porous coordination polymer(PCPs), are organic-inorganic compounds which are self-assembled from metal ions/clusters with organic ligands attaining permanent pores, ultrahigh surface area and infinite structure tailorability. These unique properties have rendered MOFs as great candidates in gas adsorption and separation, catalysis, sensing, drug delivery, etc. Structural control over both the molecular level and particle level is believed to be an efficient way for both creating new properties and enhancing the current performance of MOFs. To further developing the properties of MOFs, MOFs particles were modified through various techniques to achieve the goal above. Techniques, including self-assembly, were applied to make structure based new or enhanced properties of MOFs.

For the first part of this thesis, a route for the synthesis of monodispersed MOFs particles was developed and the MOFs particles were further assembled to large area 2D/3D-ordered structures. A photonic sensor based on self-assembled MOF particles was fabricated. Control over size and shape of MOFs particles is important in the synthesis of MOFs. However, synthesis of monodispersed MOFs particles is still not well understood. At the same time, monodispersed particles are excellent building blocks for superstructures in bottom-up routes. This lack of monodispersed MOFs particles has hindered research on self-assembled MOF superstructures, preventing researchers from developing and studying possible, novel properties of MOFs. Herein, we chose acetic acid as the modulator for the synthesis of monodispersed MOFs. These monodispersed MOFs particles were further self-assembled into 2D/3D superstructures. Also, a photonic sensor was fabricated based on the superstructure using the Langmuir-Blodgett method. The sensor responds to various hazard gas vapors, allowing people to differentiate between the vapors simply by sight. Furthermore, as a representative method of a bottom-up strategy, self-assembly has few requirements for equipment and time, making the entire process of fabrication more convenient and low-cost.

In Chapter 4, we introduces another synthetic route to control the shape of a famous MOF, HKUST-1, and its corresponding transformation to a metal sulfide as well as its applications to lithium-ion batteries. HKUST-1 is well known for its robust structure and high surface area. This time, two different modulators, oleic acid and polyvinylpyrrolidone (PVP), were chosen to tune the size of HKUST-1 particles. Fine cubic and octahedral particles were synthesized. We further utilized CuS hollow particles templated from HKUST-1 as an electrode material in lithium-ion batteries. The porous nature of MOFs derived CuS makes them excellent candidates for solving the volume changing problem in lithium-ion battery. It contributes to better stability and capacity of the battery. The transformation process is also a fast, single step, leading to more possibilities for further applications in industry. This process is also general, which should be able to be expanded to other MOFs, such as the cobalt MOFs, ZIF-67.

The last part in this thesis describes a simple and green method for the synthesis of mesoporous and yolk/shell structured MOFs. Though MOFs possess very high surface area, the pores in MOFs are usually in the micro regime. The micropores are not suitable in some situations because the micropores will limit the diffusion of molecules outside of MOFs. For example, MOFs are able to catalyze reactions even with their micropores. However, if the MOFs instead have meso- or macropores, the reaction rate will be largely enhanced. On the other hand, another advantage of MOFs in catalysis is the rigid structure, which will ensure that molecules larger than the pore aperture will not pass through MOFs. Therefore, the rigidity of the MOFs introduces selectivity into catalytic reactions. Macroporous MOFs cannot be directly synthesized by simply enlarging the ligand size. Furthermore, large pore sizes in the macro- range will result in the loss of selectivity of MOFs. Increasing the diffusion rate and maintaining the selectivity of MOFs are still quite challenging in the synthesis of MOFs. Mesoporous MOFs are potential candidates for solving this problem. Because of the abovementioned advantages of mesoporous MOFs, many methods for synthesizing them have been developed. The direct route is based on the synthesis of MOFs with larger metal clusters and organic ligands, but the limitation is that, via this route, the

synthesized MOFs usually show low stability and interpenetration in structures, which confine the applications of these MOFs. At the same time, synthesis of large organic ligands requires complex synthetic steps. Another concern is that the templates, most of which are surfactants or polymers, are not environmentally friendly. A one step, template-free method for synthesis of mesoporous MOFs is thus introduced in this part. The mesoporous MOFs obtained from this method both exhibited much higher catalytic activity and kept the same selectivity as microporous MOFs. Moreover, the method also introduced a new route for yolk/shell structured MOFs, which was difficult to synthesize via existing methods. The method developed here was believed to provide insights for the preparation of mesoporous MOFs and yolk/shell MOFs in the future.

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Abbreviations

1,4-NDC	1,4-naphthalenedicarboxylic Acid
2,6-NDC	2,6-naphthalenedicarboxylic Acid
BDC	Terephthalic Acid
BET	Brunauer-Emmett-Teller
BPDC	4,4'-biphenyldicarboxylic Acid
BTC	Benzene-1,3,5-tricarboxylic Acid
CV	Coefficient of Variation
EC	Ethylene Carbonate
FESEM	Field Emission Scanning Electron Microscope
HRTEM	High Resolution Transmission Electron Microscopy
LB	Langmuir-Blodgett
MOFs	Metal-Organic Frameworks
NH ₂ -BDC	2-amino-1,4-benzendicarboxylic Acid
NMP	N-methylpyrrolidone
NPs	Nanoparticles
PDMS	Polydimethylsiloxane
PVA	Poly(vinyl alcohol)
PVDF	Poly(vinylidifluoride)
PVP	Polyvinylpyrrolidone
PXRD	Powder X-ray Diffraction
SAED	Selected Area Electron Diffraction
SD	Standard Deviation
SDS	Sodium Dodecyl Sulfate
SEI	Solid Electrolyte Interface
SEM	Scanning Electron Microscopy
SPR	Surface Plasma Resonance
TAA	Thioacetamide
TEM	Transmission Electron Microscopy
TGA	Thermogravimetric Analyses

UV-vis	Ultraviolet–visible Spectroscopy
XRD	X-ray Diffraction

Chapter 1

Introduction

In this introduction chapter, an overview of the thesis is provided. It contains Hypothesis and problem statement ; Objectives and scope; Dissertation overview Findings and outcomes/originality. The information in this chapter will help you for understanding the motivation of my Ph.D. works and also the brief results of my works.

1.1 Hypothesis/Problem Statement

Since MOFs are increasingly important in the field of porous materials, the studies on MOFs' structures are quite important for fundamental sciences and applications. Though most of the studies are in the field of ligands and metal clusters in MOFs, we believed that investigation on structures beyond the molecular level are also important. And more findings could be found in the following aspects:

- 1) The growth of MOFs colloidal crystals with regular shapes and sizes should be achieved by the effects of modulators. These crystals would be the basis for self-assembly and other applications.
- 2) The new functions of MOFs could be developed through structures over molecular level. Such as using self-assembly for fabricating MOFs' superstructures and their applications in sensing. Overcoming the diffusion problem by post-synthesis of mesoporous and yolk-shell MOFs.

1.2 Objectives and Scope

The purpose of this work is to develop the controlled synthesis of MOFs over size, shapes and arrangements, from single crystal to superstructures, all of them accompanied with new properties. Though the study on the controlled synthesis of MOFs has attracted increasing attentions, the synthesis of monodispersed MOFs crystals is still quite the challenge. Since monodispersed particles are basic building blocks of superstructures, the lack of monodispersed particles will severely limit the building of MOFs superstructures. As discussed in the introduction, superstructure of NPs show enhanced properties or even novel properties beyond the single NPs. The fabrication of MOFs superstructures are believed to be a crucial route to create new functional MOFs. Moreover, the utilization of unique structures of MOFs for the synthesis of other materials make it possible to generate novel structures with enhanced properties. Even the changes inside a single

crystal will bring enhanced properties which are mostly achieved by simply adjusting the metal ions/clusters or ligands. The utilization of tailorable structures of MOFs on multiple scale will improve these functionalities. In my PhD work, the exploration of MOFs' structures and the novel properties based on these structures from sub-single crystals to assembled superstructures are presented here. The following points will bring more details about this work:

First, the synthesis of monodispersed MOFs crystals using added modulators during the reactions is described. The monodispersed crystals were self-assembled to 2D and 3D superstructures via proper methods. Furthermore, the assembled MOFs could be utilized as photonic sensors for various chemical vapors.

Second, cubic and octahedral HKUST-1 particles were synthesized using different modulators added in the solvothermal reactions. A general strategy towards transferring MOFs to metal sulfides hollow particles with porous shell was developed. These particles exhibited excellent performance when evaluated as electrode materials in lithium-ion batteries.

Third, template-free method for the synthesis of mesoporous MOFs and yolk-shell metal oxide@MOFs was developed. When using the mesoporous MOFs and yolk-shell MOFs as platforms for encapsulated NPs in catalysis, both mesoporous and yolk-shell MOFs exhibited enhanced activity because of the increase in the diffusion rate of reactants. Moreover, mesoporous MOFs and yolk-shell MOFs still provided size selectivity in the reactions.

1.3 Dissertation Overview

The thesis includes seven chapters. Chapter 1 provides the scope and overview of the whole thesis. At the same time, the Through chapter 1, one can get the brief information from all aspects of this thesis.

Chapter 2 mainly provides the background information of this thesis, introducing various

porous materials, ranging from porous carbon to silica and zeolites. Compared to traditional porous materials, MOFs possess charming properties based on the unlimited possibilities of available structures. Moreover, the MOFs can be designed according to different applications. At the same time, the applications of MOFs are also presented in the introduction. MOFs find their applications in various field including gas storage/separation, catalysis, drug delivery, sensors and etc. Self-assembly of nanoparticles has also been summarized to shed light on the following works of the self-assembly of MOFs particles. Self-assembly provides a convenient way to synthesize functional superstructures over signal particles' level. From the information in chapter 2, we believed by correlating self-assembly with colloidal MOFs crystals more functional MOFs will be developed. And also the existing problems in current MOFs could be solved by modification MOFs beyond molecular level.

In chapter 3, the main experimental techniques are introduced. Since choosing proper techniques for the synthesis and fabrication of target materials is quite important for the final applications. The right characterizations of synthesized materials will also help us better understanding our results. Combined the proper techniques, we will able to enhance the materials and make them better and more suitable for real applications.

Chapter 4 describes a method for the synthesis of monodispersed MOFs particles via modulation route. The as-prepared MOFs particles were further self-assembled into 2D and 3D structures. The assembled MOFs particles are able to perform as photonic sensors for gas vapors. Furthermore, the signal can be seen directly by eye without the need for complicated signal transaction processes.

In chapter 5, cubic and octahedral HKUST-1 crystals were synthesized by adding oleic acid and PVP correspondingly. Then the HKUST-1 crystals were further transferred to hollow metal sulfide particles via a simple solvothermal route. The hollow particles showed excellent performance when evaluated as electrode in lithium-ion batteries.

In chapter 6, we mainly developed a template-free method for the synthesis of mesoporous MOFs and yolk-shell MOFs. It is well known that, though MOFs are popular platforms of supporting active functional nanoparticles, the diffusion rates of reactants into MOFs are usually restricted by their small pore apertures. Thus, mesoporous MOFs will circumvent this problem. However, traditional routes utilize templates during the

synthesis of mesoporous MOFs which have associated problems such as the elimination of templates and the difficulties of scaled-up. The new method doesn't require any templates for the synthesis of mesoporous MOFs. Also, through this method, MOFs with yolk-shell structure were synthesized. Both the mesoporous and yolk-shell structured MOFs show better activity than pure MOFs in the catalysis.

The final chapter will introduce some not finished works. And based on the current work and information, proposed future works in this area is presented.

1.4 Findings and Outcomes/Originality

This research led to several novel outcomes by:

1. Establishing a synthetic route for monodispersed MOFs colloidal crystals.
2. Establishing a general strategy for synthesis regular shaped HKUST-1 crystals.
3. Self-assembly of 2 dimensional and 3 dimensional superstructures of MOFs.
4. Correlating self-assembly with MOFs crystals and fabricating a chemical vapor sensor based on their assembled super structures.
5. Developed a general transformation route from MOFs to hierarchical hollow metal sulfide particles.
6. Developed a template-free route for mesoporous and yolk shell MOFs.

Chapter 2

Literature Review

In this chapter, the background of this thesis is summarized. And this chapter is divided into two parts: one is on MOFs while the other on self-assembly. Current progress and existing problems in these areas are introduced. The literature review here will help readers understand the motivations and meanings of the works on self-assembly of MOFs.

2.1 Porous materials

2.1.1 Porous carbon

Porous carbons^[1] are important members in porous materials since they possess high surface area, large void volume, strong mechanical strength and excellent stability under both harsh chemical and thermal conditions^[2]. These distinguished properties ensure their wide applications in gas storage and separation, batteries, molecular sieving, catalysis and absorbents for oil and other hazard materials^[2]. The most popular synthetic route of porous carbons is the direct carbonization of starting materials and^[3] followed by an activation process. Many kinds of porous carbons, both microporous and mesoporous, are prepared by template methods. The templates are various, including compounds from common surfactants to inorganic particles. Porous carbons have been widely used in industrial fields as well, microporous carbons are suitable for the adsorption of small gas molecules while mesoporous carbons perform better with large molecules fields, for example polymers and dyes. The mesopores in carbons have also been proved to be an advantage in new applications, such as electric double-layer capacitors.

2.1.2 Porous silica

Porous silica are another series of very attractive porous materials based on their high stability, adjustable pore sizes and low toxicity for human. Similar to porous carbon, microporous silica are mainly applied in the fields of gas separation, catalysis, coating materials and electronic devices^[4]. However, the size of the micropores limits their applications with large molecules^[5]. Considering this point, mesoporous silica are able to act as carriers/cargos for drug molecules, dyes and biological molecules^[4]. This introduction here will mainly focus on mesoporous silica with a pore size from 2nm to 50nm. The synthetic routes of mesoporous silica are well-developed, and, among these methods, two of them are most commonly used. The first one is based on the solution route^[6], where surfactants are added into tetraethyl orthosilicate (TEOS). After addition, the surfactants form micelles which work as templates for mesopores. The final products can be simply obtained from the calcination of as-prepared samples to eliminate the surfactants. Instead of solution methods, self-assembly^[7] is a powerful tool for the

synthesis of mesoporous materials. Mixing very low concentration silica with surfactants first and then evaporating the solution results in an increased concentration of silica and also jumpstarts the self-assembly process. Using the two methods, however, only limited kinds of mesoporous silica have been synthesized to date. The use of large amounts of surfactants also causes environmental problems.

2.1.3 Zeolites

Zeolites^[7b, 8] are three dimensional porous materials formed by aluminosilicates in a highly crystalline state. Some of the zeolites are natural products while the mostly widely commercialized zeolites are synthesized. Natural zeolite occur in volcanoes where ash layers or rocks react with alkaline water. Artificial zeolites, on the other hand, are synthesized by the slow reaction of a silica-alumina gel in alkaline conditions^[9]. Zeolites have regular pores and cavities crossing their structures, but they are much smaller when compared with mesoporous materials. Porous zeolites, however, are still very promising in real applications such as cation exchangers, compact detergents and radioactive waste management^[10]. The most famous application is working as catalysts in industry^[11]. One of the best examples gasoline: the majority of the gasoline is produced through a cracking reaction in which zeolites are the catalysts. The highly stable structures, highly active acidic catalytic centers, easy use and recyclability as well as good shape and size selectivity have made zeolites a superstar in petro-chemical industry since the 1960s. Although zeolites have supreme properties, however, they are difficult to design. The harsh synthetic conditions also make it difficult to modify the structure of zeolite. The slow diffusion of reactants due to the small sized pores is another disadvantage of zeolites. Thus, developing of more flexible zeolite are restrained by the abovementioned aspects.

2.1.4 Metal-organic frameworks

Metal-organic frameworks (MOFs)^[12] are inorganic-organic hybrid materials which possess the advantages from both their inorganic and organic components(Figure 2.1). Considering the advantages, the inorganic aspects endow MOFs with rigid structures while the organic part allows MOFs to attain tailorable structures. When both inorganic

and organic parts are combined, MOFs show ultrahigh surface area and nearly infinite structural possibilities. Yaghi et al.^[13] reported a MOF with an ultrahigh Langmuir surface area up to $10400\text{ m}^2\text{ g}^{-1}$. To date, MOFs have been widely studied in gas storage/separation^[14], especially in hydrogen storage since hydrogen is a clean energy source with high energy density. Moreover, MOFs also exhibit applications in sensing^[15], catalysis^[16], drug cargos^[17], lithium-ion batteries^[18] and other fields^[19]. Aside from the current applications of MOFs, the existence of MOFs highlight the incredible possibilities of the combination of inorganic and organic chemistry, which were thought to be immiscible before. One of the first applications of MOFs is gas storage because the ultrahigh surface area and potential scalability make them promising materials in this area. Hydrogen storage in MOFs was reported decades ago, with the highest excess hydrogen storage of MOFs was reported by Hupp et al in Northwestern University, NU-100, which reached a capacity of $99.5\text{ mg}\cdot\text{g}^{-1}$ under conditions of low temperature (77 K) and high pressure (56 bar)^[20]. The highest total hydrogen storage capacity that has been achieved to date is $176\text{ mg}\cdot\text{g}^{-1}$ from MOF-210 at 77 K and 80 bar^[13]. Another important gas is CO_2 , because CO_2 is the most important greenhouse gas.

Figure 2.1. Schematic illustration of the growth of MOFs comes from the combination of metal ions/clusters with organic ligands. And by designing different ligands to achieve different

structured MOFs. a) and b) represent the most popular Zn and Cu based MOFs correspondingly. (Reprinted with permission from 21)

Figure 2.2. Scheme of engineered core–corona porous iron carboxylates for drug delivery and imaging. (Reprinted with permission from 37)

The capture of CO₂ in MOFs does not only rely on the high surface area but also the modification of MOFs. MOFs have functional groups, usually amino group(-NH₂)^[21], showing much better adsorption of CO₂. In the field of gas separation, MOFs can be directly applied to analytical chemistry and potential commercial petro- industry^[22]. As a platform in biomedicine^[17, 23], MOFs have very high loading of drugs accompanying with other functions, such as MRI contrast agents(Figure 2.2). The suitable pore sizes allow

MOFs to host large molecules and imparting controlled release properties at the same time.

Fabrications of MOFs thin films are coming into the field of vision in recent years and show their significances both in research and real applications^[24]. The applications of MOFs thin films are growing quickly, especially in chemical sensors^[25] and continuous separation^[26]. The prevalent methods usually require supporting materials as substrates^[27], such as silicon, glass and metal, and then preparing the MOFs thin films directly on it. However, most MOFs thin films have their own reaction conditions in different techniques, including Liquid-Phase Epitaxy^[28] and Langmuir-Blodgett (LB)^[29], and only grow on certain substrates. Substrates provide extra strength to MOFs thin films since the thin films themselves are usually not strong enough in some applications. However, because of the difficulties faced in fabricating MOFs thin films, MOFs thin films are still far behind the achievements in other fields of MOFs, which are growing faster than ever before^[24]. Many functions of thin films cannot be replaced by only using MOFs particles.

Figure 2.3. Photograph of a series of ZIF-8 films of various thicknesses grown on silicon substrates, which can be used as selectively gas sensors. (Reprinted with permission from 40)

MOFs-based sensors can be mainly divided into two parts, photonic^[25b](Figure 2.3) and luminescent structures^[19b]. The sensors based on luminescent structures usually require modification on a molecular level and also respond to certain molecules^[19b]. The signal transduction of luminescent MOFs rely on the quenching process when the MOFs meet corresponding molecules. The MOFs sensors based on photonic structures can mostly be fabricated via bottom-up approaches, which are more convenient. Moreover, the signal of photonic MOFs sensors can be directly read out because they show significant color change when exposed to the materials they are designed to detect. Photonic MOFs sensors are also able to detect various molecules instead of certain molecules of

luminescent MOFs sensors. But MOFs sensors based on luminescence will show a better detection limit. Deciding which MOFs sensor should be used should highly depend on the real situations in which the sensors will be applied to.

In catalyst, MOFs are able to work as catalysts in reactions by themselves. The introduction of unsaturated metal sites^[30] and functional organic ligands^[31] during the synthesis of MOFs provide MOFs with enormous catalytic active centers. Another strategy is using MOFs as platforms in catalysis since their unique structures not only will increase the stability of guest active materials but also will impart additional selectivity into the whole system^[32]. For example, nanoparticles (NPs) are well known catalysts but they suffer from aggregation and thus lead to the loss of activity during the reactions. Extra supporting materials enhances the stability of nanoparticles^[33]. Incorporating NPs into MOFs extends the lifetime of active catalysts because the confinement in space provided by the MOFs protects NPs from aggregation. Moreover, the rigid apertures of MOFs pores also introduce extra size selectivity during catalysis reactions^[34]. The NPs@MOFs show activities both from the frameworks and the guest NPs, and synergy between the two components makes the composite more promising in catalysis. For example, the composite could catalyze the hydrogenation, oxidation and condensation reactions^[35].

2.2 Synthetic strategy of colloidal MOFs

2.2.1 Modulators

The most convenient strategy for synthesizing MOFs is the solvothermal route because only a few simple steps are required for the reactions involved. Some MOFs can be directly synthesized as colloidal particles through the fine tuning of reaction parameters (concentrations, solvents and temperature)^[36], but better control over both the sizes and shapes of MOFs still requires additional techniques or the introduction of modulators during the reactions. Polymers^[37] and mono-carboxylic acids^[38] are usually used as modulators in the synthesis of colloidal MOFs. The mechanism of the mono-carboxylic acid route is ascribed to their competing abilities with the ligands during the reaction. The mono-carboxylic acid binds to certain surfaces of MOFs, leading to the anisotropic

growth of MOFs. Polyhedral HKUST-1 colloidal particles were synthesized by adding oleic acid during the reaction under microwave heating^[38b]. As for the polymers, the interactions between polymers and metal ions/clusters influence the growth of MOFs particles. Polymers also interact with the ligands during this process. F127 is able to modulate the sizes and shapes of MIL series MOFs^[37]. Some surfactants, such as CTAB, will also act as modulator in the synthesis of MOFs. Finely shaped ZIF-8 particles are also achieved by adding CTAB during the hydrothermal reactions^[39]. MOFs particles with fine sizes and shapes in the colloidal realm have increasingly drawn attentions based on their wide potential applications in various fields. However, precise control of both sizes and shapes of MOFs particles is still not well studied since the difficulties in choosing the suitable synthetic parameters.

2.2.2 Templates

Using templates during the growth of MOFs crystals represents another simple route in the synthesis of MOFs colloidal particles^[40]. Both hard templates and soft templates are applied in the synthesis. For the hard templates, the growth of the MOFs particles is usually confined on the interface between solid and liquid which is introduced by the templates. The most straightforward methods for achieving MOFs colloidal particles is using active spheres to attract the precursors' nuclei on the surfaces and then crystallization. Mesoporous silica spheres are reported to be used as the active materials for the growth of ZIF-8 particles around them^[41]. The thickness of ZIF-8 can be well controlled, from 180 nm to 550 nm through multiple synthetic processes. The growth of ZIF-8 on mesoporous silica spheres changes their surface properties from hydrophilic to

Figure 2.4. Conceptual illustration of synthetic strategies for structuring of MOFs. left) hard templates and right) soft templates. (Reprinted with permission from 60)

hydrophobic due to the nature of ZIF-8. Pd@Cu₂O core-shell nanoparticles were covered by ZIF-8 on the surface of Cu₂O. Then, the Cu₂O was etched away and a yolk-shell structured NPs@MOFs was synthesized^[42]. The ZIF-8 shell was around 100 nm in size. The ZIF-8 shell provided extra selectivity in the catalysis reaction of hydrogenation of ethylene^[42]. Compared with the hard templates, soft templates, usually surfactants, formed micelles during the synthesis of MOFs. Though similar surfactants such as CTAB can be added in the reaction, the purpose here is not the same as above mentioned modulators: soft templates will self-assemble to certain structures first and crystallized MOFs will then attach to these structures. Huo and co-workers reported the Pickering emulsion of MOFs^[43]. The particles stabilized the water-oil interface, which consisted of 350 nm ZIF-8 crystals. Other MOFs such as MIL-101 and UIO-66 also worked in this system which demonstrated the generality of the mechanism. A one-step method for achieving such MOFs was reported by Zeng et al.^[44]. The complex steps during a typical multistep synthesis introduce more uncertainty and make these types of synthesis difficult to control. They synthesized a hollow structured Fe-MOF by adding the emulsifier Tween-85 (polyethylene sorbitan trioleate) into the precursors. The MOFs particles formed after the system was heated for a short time, and then MOFs particles stayed at the interface in the emulsion. Eventually, a single layer shell consisting of MOFs particles was generated. The size of the shell could be simply modulated by the concentration of the emulsifier^[45].

Gas can also be able to work as templates for directing the synthesis of MOFs. Hollow Zn-based MOFs have been successfully made by CO₂-ionic liquid interfaces. Other templates including higher dimensional structures: AAO^[46], ZnO nanorod arrays^[47] and even graphene oxide^[48], would change the growth of MOFs to a more confined structures in a similar way.

2.2.3 Reaction confinement

Confinements from the interfaces of various phases during the reactions provide synthesis of MOFs with suitable spaces. An example of such confinement is using spray-drying to generate MOFs with different structures and components^[49]. The microdroplets confined the reaction so that it only occurred inside or on the surface. During the evaporation process, the concentration of precursors will increase. Once the concentration reached the required value, MOFs will crystallize in the microdroplets. Interestingly, the MOFs tended to nucleate on the surface of the droplets instead of inside them and finally hollow structures were achieved. Most MOFs are able to be synthesized through this process. Moreover, other properties of these MOFs can be well controlled as well when changing the parameters of spray-drying, such as the size of the particles. The confinement effects will also happen between liquid-liquid interface^[50]. One direct way of this is dissolving metal ions and organic ligands separately into water and organic solvents. Then the mixture of these two phases will react at the interface between the two phases. The first hollow MOFs were synthesized through this method. The products maintain the spherical structures derived from the emulsion system. The size of MOFs could also be controlled by changing the flow rates of inner and outer flows. Solid surfaces with low wettability can provide suitable platforms for confined reactions. The advantage of this method is that the crystallization of MOFs is driven by evaporation process. Combined with other techniques, the growth of MOFs can be confined on target places on solid substrates. De Vos and co-workers synthesized patterned MOFs with a pre-treated substrate^[51]. The precursors of MOFs preferred to stay in the hydrophilic instead of hydrophobic parts. Thus the synthesized MOFs crystals would only stay in the hydrophilic surfaces. Other techniques, such as atomic layer deposition^[52] and electro spinning^[53], are also reported for the applications of synthesis of MOFs.

Figure 2.5. Overview of the process of liquid–liquid interfacial reaction. a) Cut-away view of the T-junction showing details of the emulsification step. The metal-ion-containing aqueous solution (blue) flows through a tapered capillary centered in the tubing, and the ligand-containing organic solution (purple) flows around it. b) Interfacial preparation of a MOF layer using a biphasic synthesis mixture consisting of an aqueous metal-ion-containing solution (blue) and an organic ligand solution (purple). Crystallite formation takes place primarily at defects remaining in the layer, resulting in self-completing growth. (Reprinted with permission from 70)

2.2.4 Top-down process

Top-down processing play an important role in the synthesis of MOFs, though the high cost of these techniques sometimes limits the synthesis from being scaled up. However, the precise controls provided by top-down processes give them advantage over other methods. Yanai and Co-workers reported the assembly of ZIF-8 crystals under electric fields^[54]. ZIF-8 crystals formed a linear chain under the electric fields and preferred to attach to each other with (110) facets. After removing the electric field, ZIF-8 crystals still maintained these linear structures. Falcoro and co-workers proposed a convenient method for imprinting any type of MOFs thorough lithography and hot-pressing^[55]. They introduced polyhedrate zinc phosphate particles as nucleation seeds for MOFs. By controlling the position and arrangement of nucleation seeds, they achieved the arrangement of MOFs. Moreover, adding other functional molecules into the seeds would introduce the both seeds and molecules into MOFs simultaneously.

2.3 Self-assembly of nanoparticles

Fabricating nanostructures attracts enormous attentions from both the research and industry fields, because they provide a crucial foundation for other structures. Typically, fabrication methods are categorized as top-down and bottom-up approaches. Top-down approaches, such as photolithography and E-beam lithography, have been widely used and are considered to be easier methods to fabricate and manipulate nano/microstructures with large potential. Bottom-up approaches are thought to be an alternative strategy for fabricating these structures, but are limited by the facts that most available building blocks are isotropic particles in the past^[56]. Recently, developments in the synthesis of anisotropic particles have provided us with more opportunities of fabricating complex and sophisticated 2D and 3D structures, opening a bright future for self-assembly structures^[57].

In the 1970s, early works focused on the synthesis of monodispersed colloidal particles in different shapes. Since then, many achievements have been realized in the synthesis and self-assembly of these nanoparticles^[58]. In particular, photonic crystals promoted the needs for regular arrays of spheres from nanometers to micrometers range. The self-assembly of small nanoparticles(1-10nm) and large particle usually produce similar structures, and which may guide the other's assembly progress. However, the interactions between the small nanoparticles are mainly influenced by van der Waals forces while the interactions between large particles are dominated by short-range interactions^[59]. Therefore, the self-assembly processes of the two sizes differ in mechanism.

After many years' research on the synthesis and self-assembly of these nano- or microstructures, several methods were developed to fabricate these desired structures including evaporation^[60], sedimentary synthesis^[61], DNA-directed^[62], etc.^[63]. Evaporative self-assembly of nanoparticles has been recognized as a non-lithographical means of producing a diverse range of intriguing surface pattern in simple, rapid, inexpensive and scalable way. Through control of the evaporative flux, heat, substrate geometry, etc., evaporative self-assembly yields complex but ordered structures over large areas which suggests great potential applications in sensors^[64], electronic and optical devices^[65]. Furthermore, in the sedimentary method, usually a highly concentrated solution of particles were deposited inside small containers where the inside environment of the

containers is stable (Figure 2.6)^[61], isolating the inside system from outside influences. The micro- or nanometer particles in their high concentration solutions are able to spontaneously form a close packed structure when their free volume is lower than a fixed level^[66]. The final structures can be large scale and ordered with few defects even the mechanical strength is not good. To solve this problem, some new methods were developed recently. Tsutomu Sawada, et al reported a new method via using photopolymer gel to immobilize the self-assembled spheres arrays^[67]. The hydrolysis of tetraethyl orthosilicate (TEOS) also offers more robust structures through because the silica particles can connect to one another in various ways^[68]. Evaporative and sedimentary methods are very simple manners to fabricate 3D self-assemble structures and sometimes 2D structures. When it comes to 2D structures, Langmuir-Blodgett assembly^[69] is an efficient way to fabricate 2D structures or even 3D with various types.

Figure 2.6. SEM micrographs of the colloidal lattices (left) and the corresponding diagrams of their densest known lattice packings (right): a) cubes; b) truncated cubes; c) cuboctahedra; d) truncated octahedra; e) octahedra. Colour in d) and e) is used to indicate different layers of the crystal. Scale bars are 500nm. (Reprinted with permission from 84)

Langmuir-Blodgett assembly is based on the facts that amphiphilic molecules can float between two phases (Figure 2.7). When the concentration of the molecules is lower than a certain level, a molecular monolayer is formed. LB was used to self-assemble a

monolayer in a similar mechanism- changing the amphiphilic molecules to oil phase particles in solution. By dropping the oil phase slowly on the surface of water, the oil will spread on the surface, which means that the particles in the oil will spread to form a monolayer on the water surface. Compression or expansion leads to different self-assembled structures at the water-oil interface^[70]. Furthermore, the floating monolayer can be transferred to a substrate with dip coating easily. The factors during this process, such as surface pressure, substrate hydrophobicity, and transfer speed, will control the final self-assembled structures^[71].

Figure 2.7. Surfactant molecules arranged on an air- water interface which was used to illustrate the basic Langmuir-Blodgett film structures.

The goal of fabricating various self-assembled structures is to develop new properties of these specific structures is to develop new properties corresponding to those specific structures. Since many kinds of nanoparticles ranging from metal to polymer were used, the properties of these self-assembled structures differ greatly from each other. Most of the applications of these self-assembly structures focus on exploiting their templates functions as well as their optical properties^[72]. In terms of optical applications, the structures' properties relate to the size of individual particles comprising the structures, which is similar to the wavelength of visible light. In particular, each structure exhibits a specific reflection spectra governed by the lattice spacing, reflective index contrast and volume fractions of the components^[73]. When observed from different angles, the

reflection is different. The colors originate from the light's interactions with regular self-assembly structures, also are influenced by the lattice spacing. Solvents, however, will penetrate the space between these structures, changing the color. And, by filling in the space between the periodic structures with photochromic dyes^[74] or applying electric fields^[75], one can control the optical properties further. For example, a structure containing supermagnetic components was switchable based on the magnetic field^[76]. Mostly, the optical properties of self-assembly structures are sensitive to the changes in the spaces of the regular structures. This characteristic prompts researchers to develop readily modifiable materials by embedding particles in matrix. Ordered silica spheres in the hydrogel matrices were functionalized as optical sensors of different factors (temperature^[77], pH^[78], ion concentration^[79], type of solvents^[80], etc.^[81]). Other suitable matrices for embedding colloidal particles include metallopolymers^[82], elastomers^[83]. And 2D self-assembled Janus particles in which black or white pigments were separately manipulated by the rotation of Janus particles to fabricate display system driven by electric field^[84].

In addition, the hydrophobicity of substrate driven by the 2D self-assembled particles to form a superhydrophobic surface^[85]. Self-assembled structures which templates the synthesis of porous materials are widely used^[86]. Other potential applications of the self-assembled structures include nanoscale electronics, plasmonic devices and hierarchically structured catalysis^[58b, 87]. Self-assembled metal nanoparticles show great plasmonic properties. A typical phenomenon of this is the surface plasma resonance, known as SPR (Figure 2.8)^[88]. SPR was used to describe a certain type of oscillation when at resonant conditions. Free electrons clouds around the positively charged nuclei of metals were defined as delocalized electrons. When the oscillating delocalized electrons interact with the incident light, the electrons will be excited. However, the Coulombic force pulls the electrons back to their initial position. The light is then coupled to the continuous oscillation of the free electrons in the metal, and the surface Plasmon occurs. An exciting feature of surface Plasmon is that discrete materials with this phenomenon can be coupled when they are positioned in nanometer scale^[89]. Furthermore, rational structures of these nanostructures will enhance the signal to several orders of magnitude higher, making SPR detectable^[90]. Both the types of the metal^[91] and surface topography^[92] will

determine the final behavior of the resulting SPR. So the highly regular self-assembled nanostructures are extremely important in SPR-based technologies.

Figure 2.8. Scheme of local surface Plasmon resonance. (Reprinted with permission from 121)

Though some aspects of self-assembled structures were summarized in above paragraph, the enormous achievements still cannot be fully covered in this introduction. The unknown properties of self-assembled structures make the self-assembly of highly ordered nanostructure over sizes and shapes is extremely crucial to the development of many subjects and applications. Both new methods and new kinds of materials should be introduced into the self-assembly field to create novel structures with unique properties.

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Chapter 3

Experimental Methodology

The main experimental techniques which are chosen for the synthesis and characterization in the thesis are introduced in this chapter. According the properties of MOFs, the corresponding techniques such as TEM, SEM, XRD and others are presented. The reasons for choosing these experimental techniques are also explained here.

3.1 Rationale for selection of methods

Metal-organic frameworks (MOFs) are porous materials assembled from metal ions/clusters and organic ligands. Usually the pores in MOFs crystals have sizes below 2nm. Though through some particular designs or modifications, the pores' sizes can be increased to meso- or macro porous range. The majority of MOFs show microporous structures. And in the thesis, we mainly synthesized MOFs crystals with certain shapes and sizes. The size of these synthesized MOFs crystals range from hundreds nm to several micrometers. These colloidal MOFs crystals are good platforms for many guest functional materials. The MOFs crystals themselves are also promising building blocks for sophisticated structures. The complex structures of MOFs crystals find their uses in the field of sensing based on photonic properties. More than the sensing, the MOFs crystals are also high quality templates in the synthesis of other materials. The unique structures of MOFs provide templates with a regular arrangement inside. The MOFs crystals are also post modified by a simple solvothermal method for better performance in selective catalysis.

Based on the abovementioned information, we discuss the rationale for choosing corresponding experimental techniques one by one:

1) SEM

Since the MOFs crystals synthesized in the thesis are all colloidal particles, we need to use SEM to observe the shapes, sizes and other surface changes by SEM. For example, the synthesized monodispersed UIO-66 crystals need to be characterized by SEM to get the basic information on the shapes and sizes. The morphology of these MOFs crystals are important for following works on self-assembly, template synthesis and post-synthesis.

2) TEM

Researchers use TEM to help them characterize both the outside and inner part of small particles. In the thesis, we synthesized some hollow inorganic particles from MOFs. TEM will be able to make sure the hollow nature of these particles. And also for the mesoporous and yolk-shell structured MOFs, we observe these structures directly.

Under the HRTEM, we also see the lattice spacing of our materials. The SAED pattern will tell us whether the materials are crystalline or amorphous. Certain SAED patterns are used for analysis of lattice arrangement in these materials. We synthesized Pt@UIO-66 crystals, we can tell the distribution of these Pt NPs and their morphology by the TEM.

3) XRD

XRD could be used for the characterization of materials. According to the XRD, researchers are able to tell the component of the materials. In the thesis, XRD are mainly used for the justification of existing MOFs. If we got the MOFs crystals with same XRD patterns as reported MOFs, we are able to tell the whether we synthesized the right MOFs though the morphology are quite different. And if we put NPs in the synthesis of MOFs, we judge whether the NPs are combined with MOFs.

4) Surface area and porosity analysis.

MOFs are high porosity materials and the understanding of the total surface area, the pore volume and sizes are very important for their applications. And this technique will help us make sure the type of MOFs combined with XRD. Because the MOFs will collapse during the process of eliminating inside guest molecules. A non-porous coordination polymer will lose the most important nature of MOFs. The information on the pores of MOFs also help us find out the corresponding applications.

5) UV-Vis

The UV-Vis provide data of the light absorbance of materials in the visible and ultraviolet range. We fabricated a MOFs photonic sensors and UV-Vis will help us analyze the sensor performance quantitatively. The locations of absorbance peaks are important for the analysis of the structure based photonic properties.

6) Gas chromatography(GC)

For the tests of the catalysis performance of Pt@UIO-66, Pt@mesoporous UIO-66 and Pt/ZrO₂@void@UIO-66. Firstly, GC provide data about the activity of these catalyst in designed reactions. Secondly, through specially design catalysis experiments, the

integrate shells of these crystals are proved.

7) Thermogravimetric analyses (TGA)

The TGA are used for the tests of stabilities of MOFs under heating. And more than the stability, through the weight loss curve, we also certify the composition of materials by combining with other techniques.

More techniques used in the synthesis and characterization in this thesis will be discussed in the following part. The mechanism and more detail could be found there.

3.2 Synthesis

3.2.1 Solvothermal synthesis

Though many different methods have been developed for the synthesis of MOFs, the solvothermal method is still the most popular method compared with others^[1]. There is no requirement on special equipments, the reactions take place in closed vessels under heating. Some MOFs could be synthesized under room temperature. However, most MOFs need elevated temperature for the growth. And in the thesis, we need regular MOFs crystals rather than the irregular powders. The solvothermal method provides the most general strategy for the synthesis. At the same time, we are able to introduce many growth directing agents to control the growth of the MOFs crystals.

The MOFs are built from the coordination bond between metal ions and organic linkers. And in fact, MOFs are also coordination polymers but they possess pores in their structures. The tuning of the reaction conditions are easy for the solvothermal methods. Many parameters will affect the final products. To make the MOFs formed from the clear solutions of metal ions and ligands, the concentrations of the precursors must be higher than the critical nucleation concentrations. It will be achieved usually by increasing the temperature. Other parameters, such as the speed of changing the temperature will make differences on crystals' size. Commonly, slowing down the cooling of the reactions, researchers could get larger particles.

Solvents are the most important part in the synthesis of MOFs crystals. They are not only the medium for the reactions but also support the porous structures of MOFs. It is the reason that upon eliminating the solvent molecules inside MOFs crystals, some MOFs will lose their porous structures. A successful synthesis of MOFs requires the chosen of proper solvents. Sometimes, the same starting metal ions and ligands in different solvent will result into different MOFs^[2].

Figure 3.1. Summary of strategies for manipulating the crystal growth, i.e., size and morphology of MOF crystals. (Reprinted with permission from 1)

Instead of solvents molecules are trapped in the pores of as-synthesized MOFs crystals, the unreacted linker molecules sometimes will also be trapped during the growth^[3]. Interestingly, because of the strong interactions between the guest molecules and the frameworks, the MOFs here show flexible frameworks, which could be switched between small and large pores. It also happened in the benzene during the synthesis of pillared-layered MOFs^[4]. Some surfactants also will interact as structures directing agents, F127 and CTAB are used for the synthesis of mesoporous MOFs^[5].

In Figure 3.1, the different routes for the synthesis of MOFs crystals are summarized. Apart from the abovementioned methods, the temperature programming also influences the growth of MOFs crystals. In the synthesis of HKUST-1 crystals, the growth progress is divided into three steps: incubation of precursors, nucleation and crystals growth^[6]. Programming the temperature will result in various HKUST-1 crystals.

The enormous reaction parameters in the solvothermal synthesis of MOFs give us enough room for the modulation of MOFs products. Considering the conveniences and generalization of this method, we chose solvothermal method for the synthesis of MOFs.

3.2.2 Langmuir-Blodgett (LB) film

The name of Langmuir-Blodgett film comes from Irving Langmuir and Katharine B. Blodgett since they invented this technique. The LB film contains one or more layers of materials on the water-air interface. The films are able to be deposited onto solid supporting materials by immersion. The thickness of these monolayers are identical based on the compositions.

A typical LB film forms when amphiphilic molecules stay at the interface of air-water. The mechanism can be explained as the minimization of the surface energy. Surfactants are used here for an example, the hydrophobic parts favor stay away from water while the hydrophilic parts contact with water. The arrangement of these surfactants will reduce the surface energy in the system.

If the concentration of the surfactant is less than the critical micelle concentration, the surfactants will behave like free motion on the interface. They perform similar with ideal gas molecules in an independent system. Surface area, surface pressure and number of surfactant molecules describe the state of the system (Figure 3.2). When the surface pressure or numbers of surfactant increase, the surface area will decrease. A real situation is when pressing or increase the amount of surfactants added in the system, the area of the whole film will be smaller. The compressed film behaves more like "liquid" or "solid". A close packed film will form when applied an enough force.

The LB techniques are popular in the preparation of thin films and other complex structures^[7]. The prepared LB samples find their applications in many fields, such as optical, biological and semiconductors. For example, the LB technique is used for preparing an artificial biological membrane. Since the lipid molecules are also similar with surfactant-long carbon chains with polar heads. An extremely thin film can be made by this technique and these films are promising model for the study of biological interactions between active materials and the membrane^[8].

Figure 3.2. The condition of Langmuir-Blodgett film depends on the surface pressure.

3.3 Characterization

3.3.1 Scanning electron microscope (SEM)

The SEM is based on the signals of electrons interacting with samples. The signal contains the information about the topography and composition of materials. The resolution of SEM can be down to 1nm. And specimens can be observed both under high vacuum and low vacuum. An environmental SEM is able to be used for scanning a wet sample. The signal of SEM can be divided into many different types; detection of secondary electrons generated from the electrons beam focused specimen is the most popular mode. Many factors are able to affect the secondary electrons (SE).

Apart from the secondary electrons, signals such as back-scattered electrons (BSE), characteristic X-rays, cathodoluminescence (CL), specimen current and transmitted electrons. Not all the SEM can detect the above signals. However, the most common SE is the standard signal for SEMs. The signals come from the interactions when the electron beam heats the specimens. The images generated by the collection of these electrons with

or near the surface of specimen. Under the secondary electron imaging (SEI) mode, SEMs will achieve a very high resolution images.

Not like SEI, the BSE generate from the elastic scattering when the electron beam heats the sample and bounce back. And the signal of BSE is highly based on the atomic number of the materials. So the BSE was used for detecting the distribution of different elements in a specimen. Sometimes when different kinds of materials mixed together and the sizes of these materials are small for detection under SEI, BSE is a better choice. BSE could be used for detection of colloidal gold NPs in biological samples.

Since the MOFs crystals we synthesized are mainly distribute from 100nm to 1um, the SEM is very useful for the characterization. A standard SEI mode SEM is enough for the morphology detection of MOFs crystals.

The MOFs are non-conductive and the requirement for a SEM specimen is electrically conductive. Before doing the SEM, the MOFs crystals need to be sputter a nm thick metal layer in case of the electron accumulation on the surface of MOFs. Once the electrons accumulate on the specimen, researchers won't able to get sharp images of these specimens. Lots of faults and artifacts will show on the images because of charging. Usually the coated metal are Au or Pt, since their high stability and good electrically conductivity. For the biological samples, if the specimen can't be dried during the observation such as living cells, a cryo SEM is better for living specimen.

Figure 3.3 illustrates the basic structure of an SEM. The electron beam comes from the electron gun. The most common type of the electron gun is a tungsten filament since they are stable under high temperature which allow them to be heated for electron emission. Another reason is that the low cost of tungsten filaments.

After the emission, the electron beam usually will pass through two condenser lenses (Figure 3.3). The beam spot size after the condenser lenses is about 0.4-5nm in diameter. Then the electron beam is deflected through the deflection coils to make the beam in the x and y axes for the scanning.

Figure 3.3. schematic of an SEM

When the electron beam first arrives at the sample, the electrons are scattered and absorbed by the sample. The energy exchange happens during the process where high energy electrons are reflected by elastic scattering while emission of secondary electrons by inelastic scattering. All the signals are detected by corresponding detectors. Then the detected signals are transferred into digital information on the computer screen.

Detection of secondary electrons is the most common mode for SEMs. These electrons are generated by inelastic scattering with the samples. They are only a few nanometers from the surface since the low energy of these electrons. Then the electrons are detected by the Everhart-Thornley detector. After the acceleration process in the detector, the energy of them is strong enough to cause cathodoluminescence. The signals are further conducted to digital images on the screen. The morphology of the sample is achieved by the contrast on the images. Usually steep and sharp parts of the sample are brighter than the flat surface since on the sharp part the electrons will be emitted more because of the incident angle making the escaping route shorter.

More functional SEMs are developed based on real uses. Transmission SEM is made by adding a special detector in a common SEM. The Transmission SEM can be used for simple purposes of internal structures. 3D SEM is also developed for better acquiring the

whole surface details of specimens. Environmental SEM (ESEM) is made for use on observing wet samples. ESEM is very useful on biological samples and other wet samples. Based on above information, SEM is essential for characterization of MOFs colloidal crystals. We are able to get the morphology information about MOFs to help us synthesize fine controlled crystals over size and shape.

3.3.2 Transmission electron microscopy (TEM)

Similar with the SEM, TEM also collects the information from the interactions of the electron beam with specimen. The different point is TEM gets the signal after the transmission of electrons. TEMs have better resolution than SEMs' which makes them qualified for the characterization of single atom. In both biological and physical fields, TEMs show their applications from virology to semiconductors. The TEMs are used here for the characterizations of NPs@MOFs crystals and other structured MOFs such as mesoporous and yolk shell MOFs as well as MOFs derived particles. The high resolution will make sure we can get more details on the MOFs structures. For the MOFs crystals with NPs embedded in them, which cannot be observed by SEM, TEM will show information inside the MOFs crystals. The structures of a basic TEM is shown on Figure 3.4. From top to bottom, the arrangement are like follows: electron gun(the generation of electron beam), different lens and apertures(confine and enhance the signal) and the imaging system.

The tungsten filament or a lanthanum hexaboride (LaB_6) is used for the generation of electron beam in TEM^[9]. The tungsten filaments are usually in hairpin or spike-like shape. While LaB_6 sources is in single crystal form. After applied a high voltage sources, the emission happened. Wehnelt cylinder is used for the focus of electrons into a beam. The electron beam is will be further focused by the upper lenses in TEM^[10]. Inside the TEM, the electron beam is mainly controlled by the electromagnets and electrostatic field. The electrons inside a magnetic field will follow the left hand rule. The electrostatic fields will cause the electrons deflection along a certain angle. The combination of two fields will provide sufficient control for the electron beam in TEM.

Figure 3.4. Schematic illustration of the structures of a basic TEM.

A vacuum system which is not included in Figure 3.4 is very important for the TEM. The basic idea for the high vacuum system is to increase the mean free path of electrons -gas interactions. The low vacuum will result in the generation of arc between the cathode and the ground and the severe loss of the electrons inside the TEM. The deposition of gas molecules on the specimen will also happen. A precise high vacuum system is essential for the whole TEM.

The electron lens are made for the mimic of optical lens. The basic mechanism was discussed before. The electron lens are made of iron, iron-cobalt or nickel cobalt alloys.

And usually the electron lens consist of magnetic coil, the poles and pole piece and the yoke. The magnetic coil is used for the generation of magnetic fields and high voltage is applied on it. The insulation between wires is important since any contact will cause short circuiting.

Apertures are metal discs. The aim of aperture in TEM is to block the high angle electrons which generated from unwanted situation. And the apertures also provide a suitable way to decrease the strength of electron beam when we want to observe sensitive samples. The apertures' sizes should be chosen based on the samples and the magnifications for a better image.

The bright field imaging is the most common mode for TEM. The contrast under this mode comes from the different interactions between electrons and sample. A high atomic number material will block more electrons as well as thicker sample under this mode. This mode is also the most useful mode in our research. The NPs@MOFs crystals will show contrasts based on the NPs usually are high atomic number materials while MOFs are not. And since the MOFs crystals are porous materials, the density of NPs is higher than MOFs, which further increase the contrast. And for the void spaces in the MOFs, it is white under the TEM.

The selected area diffraction in TEM can be used for characterization of materials. It is achieved by adjusting the magnetic lenses. Firstly, the technique could be used for making a distinction between single crystalline material and polycrystalline/amorphous materials. For the polycrystalline/amorphous materials, the patterns are rings while it's dots for the single crystal.

High-resolution TEM (HRTEM) is able to generate ultrahigh resolution images. The arrangement of atoms in a materials are able to be observed under HRTEM.

In this work, HRTEM and SEAD are used together for the characterization of MOFs derived hollow metal sulfide crystals. The HRTEM find out the corresponding lattice spacing of the materials. And SEAD is used for making sure the polycrystalline nature of these hollow crystals.

Beside the basic TEM, other TEMs such as cryo-TEM are also developed for different purposes. Since the low vacuum in the TEM during the observing will result into many problems and biological samples are hard to be characterized under high vacuum. The

cryo-TEM is able to be used for the biological samples to make sure they maintain their original structures during the observation.

In summery, the TEM is a very useful tool in the characterization of various MOFs crystals and hybrid crystals.

3.3.3 X-ray Diffraction (XRD)

Considering the X-ray as an wave and the crystals are able to diffract the waves along certain directions based on the regular structure of crystals. Then the diffracted X-rays are detected by sensors and the signal can be interpreted back to the original structures of crystals. The XRD is very useful for the identifying the structures of crystals.

The Bragg's law determines the mechanism of the XRD:

$$2d\sin\theta = n\lambda$$

d is the spacing between the diffracting planes, θ is the incident angle, λ is the wavelength of the incident light and n is a integer(Figure 3.5).

Figure 3.5. Basic mechanism of the XRD.

Crystals are built from regular arranged atoms and once the X-ray heat the atoms, it will be scattered. The X-rays will be scattered into different directions at a single atom level. Because the scattering happen on the location of atoms, the scattered X-ray will cancel with each other and only be enhanced in certain directions based on the Bragg's law. Based on this process, the structures of crystals can be established.

X-ray is chosen for the diffraction instead of other kinds of waves because the similar wavelength with d spacing of crystals. The similar size will make sure the diffraction strength is strong.

Powder X-ray diffraction (PXRD) is used here for identifying the MOFs crystals based on the size of synthesized MOFs. It's a fast analysis for multiple components without the requirement for precise sample preparation. The patterns of synthesized MOFs crystals are usually compared with standard patterns to identify the structures of them. And the PXRD is also useful for the detection of guest molecules in MOFs, such as Au NPs. After post treatment of MOFs crystals, the PXRD is used for determine the structure changes.

3.3.4 Surface area and porosity analysis

MOFs are highly porous materials and the porous nature is important for their applications in many fields. In this thesis, we synthesized many colloidal MOFs crystals and the analysis on the surface area and porosity of these MOFs is the basis for further studies on their structures and applications.

The surface area analysis help us identify the MOFs since XRD only identify the crystal structures but not the pores. Sometimes the crystals will own the same structures but no pores inside. Combining with XRD, the surface area analysis will make sure the successful synthesis of MOFs. Also we synthesized mesoporous and yolk-shell structured MOFs, the surface area analysis provides us the detail information of the pores. The Brunauer-Emmett-Teller (BET) and specific Langmuir surface area, pore size, and pore volume are all included in this analysis. All the analyses are conducted through the nitrogen adsorption of these samples under the condition at 77K up to 1 bar.

The surface area and porosity measurement is widely used in many fields ranging from catalyst to Pharmaceuticals. For example, the active surface area and the porous structure of catalysts have a great influence on production rates. Limiting the pore size allows only molecules of desired sizes to enter and leave, creating a selective catalyst that will produce primarily the desired product. Chemisorption experiments are valuable for the selection of catalysts for a particular purpose, qualification of catalyst vendors, and the testing of a catalyst's performance over time to establish when the catalyst should be reactivated or replaced.

Adsorption is a consequence of surface energy and bonding will be influenced by lots of factors. Commonly, when applied high pressure in the system, more gas molecules will stay on the surface of solids. The basic step is illustrated in Figure 3.6.

Figure 3.6. Steps for adsorption of gas molecules with increasing pressure.

At beginning, a few sites on the samples start to absorb gas molecules. With increasing pressure, a monolayer of gas molecules will form on the surface of solid. Then more gas molecules will fill continuously and multiple layered gas molecules form. The small pores on surfaces will be fill to full firstly. BET theory^[11] is used here to calculate the surface area here. And when pressure is high enough to make the empty space full of gas molecules, BJH calculation^[12] can be used here to determine pore diameter, volume and distribution.

The main purpose for doing surface area and porosity analysis on MOFs is to identify the porous structures of MOFs. Coordination polymers with same XRD pattern don't mean the existing of pores in them. Introduction of different modulators sometimes will also change the primary structures of MOFs. Through surface area and porosity analysis, we are able to make sure no change happen after adding modulators during the synthesis. MOFs are also platforms for supporting guest functional materials, they are able to act as molecular sieves in catalysis. The measurement of porosity will help us choose proper reactants according to their structures. Post-synthetic MOFs with mesoporous structures and yolk-shell structures will also need porosity analysis on their structures.

3.3.5 UV-Vis

UV-Vis is short for Ultraviolet-visible spectroscopy or ultraviolet-visible spectrophotometry. It analysis light in visible and UV, sometimes near infrared, ranges. It directly relates to colors of samples in the visible range. The technique deals with the transition from ground state to excited state.

The principle of UV-Vis is based on fact π -electrons or non-bonding electrons in a molecule are able to absorb energy from light for exciting these electrons to higher energy orbitals. Since light with longer wavelength has lower energy, absorbing on long wavelength light means more easily be excited of these electrons.

The machine for measuring UV-Vis is called UV-Vis spectrophotometer. Working mechanism of this UV-Vis spectrophotometer is illustrated in Figure 3.7. It measures the intensity of light after passing through a sample. After compared with blank, the ration of these two data is called transmittance. Absorbance can be calculated according to equation

$$A = -\log(\%T/100\%)$$

where A represents absorbance and T is transmittance. Other parameters such as reflectance are also measurable based on the same mechanism of transmittance. But only change measurement from passing through light to reflected light.

Figure 3.7. Schematic of UV- visible spectrophotometer.

The structure of UV-Vis spectrophotometer is illustrated in Figure 3.7. A light comes from source and pass through filter then reach samples and reference separately. After passing through, detector collects the light. The source is usually made of a tungsten filament, a deuterium arc lamp and sometimes light emitting diodes. A typical detector is a photomultiplier tube, a photodiode or a charge coupled device.

Based on mechanism of UV-Vis, it is mainly used for determining the components in analytes quantitatively. Liquids are most common state of analytes in UV-Vis tests. For example, transition metal ions can be characterized by UV-Vis since their d electrons can be excited by light in UV-Vis range. Their colors are highly depend on their species, concentrations or other anions and ligand which could interact with them. The intensity of absorbance can be used for quantitatively define the components based on Beer-Lambert law. The equation is shown as followed:

$$A = \lg(I_0/I) = \epsilon cL$$

where A is absorbance, I_0 is original intensity of incident light and I is intensity after passing through. L represents the path length through sample, c is concentration of sample and ϵ is a constant.

We fabricated photonic sensors based on self-assembled MOFs crystals. The UV-Vis is used here for better understanding properties of these sensors. Absorbance peaks of these sensors are related to size of MOFs crystals. The introduction of chemical vapor changed the reflective index of these sensors which further resulted in changing of absorbance peaks. Thus we can read color changes before and after the exposure.

3.3.6 Gas chromatography (GC)

Gas chromatography(GC) is a very common analytical method for analysis or separation in chemistry. Here, we use GC for analysis of reactants and products in catalysis where use MOFs as catalysts.

The principle of GC is similar to other chromatography. The GC separated different chemicals by vaporize them. Due to the different physical and chemical properties of chemicals in mixture, the interactions between column and them are different. Thus they will exit column at different time. Usually they are detected at the end of column. Based on time differences, we are able to get information of each pure chemical in mixture.

Other parameters such as carrier gas flow rate, length of column and temperatures can be changed to control the process.

In a typical analysis, a small amount mixture is injected into the column. Then all the components in the mixture are carried by gas flow. The molecules entered column are interact with column. The stronger the interactions, the lower the moving speed. Each type of molecules will have different time to pass through the column. When molecules arrive the end of column, detector will trap signals. The time for passing through column and amount of molecules can be collected by detectors.

The requirements of using GC is in following aspects: 1) because chemicals need to be vaporized before analysis, the component should able to be vaporized under 300 °C and stable under this temperature. 2) no salt in samples.

Usually samples are compared with standard substances to identify components of samples. In this thesis, GC is mainly used for analyzing reactants and products before and after MOFs catalyzed reactions. According to porosity analysis, we choose different reactants with suitable size. Some can pass through MOFs pores and other can't. Based on results of GC, we know whether reactants reacted. Generally, molecules with size larger than aperture of MOFs cannot react. Through result of selective catalysis reactions, we get information of MOFs: whether functional species are fully embedded into MOFs, integrated structures of MOFs and activities of functional species. For mesoporous and yolk-shell MOFs, we use GC to identify permeability of shells and evaluating activities before and after post-synthetic treatment. MOFs crystals show their premium ability than normal MOFs.

3.3.7 Thermogravimetric analysis (TGA)

TGA is a measurement for stability of materials with increasing temperature. TGA provide information about both physical and chemical changes of samples. For MOFs crystals, physical changes happen at low temperature where they loss their guest molecules inside because of heating. Chemical changes are mainly oxidation and decomposition of primary structures and ligands. The tests on thermal stability of MOFs help us find out proper working temperature in real applications. For instance, most catalytic reactions only occur at elevated temperature, when MOFs are used as catalyst in

these reactions. Choosing a proper temperature based on TGA information will make reactions efficiency without losing activities of MOFs.

The temperature of TGA usually can be increased to 2000 °C and in analysis of MOFs, we heated them to 800°C which at this temperature all components of MOFs reacted. Generally, first drop of TGA curve appear around 100°C due to loss of guest solvent molecules in MOFs. With increasing temperature, MOFs frameworks will collapse around 400°C. TGA results also can be used for identifying component. Compared TGA results with standard will help us find out whether products here are pure MOFs.

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Chapter 4

Synthesis and self-assembly of metal-organic frameworks and their applications in chemical vapor sensing

In this chapter we successfully synthesized monodispersed MOFs colloidal crystals and these crystals are further self-assembled into 2 dimensional and 3 dimensional superstructures. To demonstrate applications of these self-assembled MOFs, a photonic sensor is fabricated. The sensor showed fast response to multiple chemical vapors.

4.1 Introduction

Self-assembly of monodispersed particles is a convenient way to functionalize the existing systems with extra properties beyond those existing in single particles^[1]. It is popular to self-assemble various particles with different size ranges. Current reports of self-assembled structures cover from metal nanoparticles to micrometer sized polymer or inorganic particles.^[2] Though most of them are spherical particles^[2], anisotropic particles^[3] are also investigated by researchers recently due to their unique functions. However, reports on self-assembly of MOFs crystals are still rare^[4]. Because the shortage of monodispersed MOFs crystals limit the availability of resources for self-assembly. MOFs are synthesized by the combinations of metal ions and organic ligands via coordination bonds. Modulating the synthesis via adding suitable modulators is a kind of efficient way to control as-prepared MOFs crystals. And the parameters of MOFs crystals will have significant impacts on the functions of MOFs.

Among various applications of MOFs, sensing^[5] has attracted increasing attentions because of the nature of MOFs, high porosity, easy tailorability and designable structures, render them promising in the field of sensing. According to the mechanism of MOFs sensors, they are mainly divided into two kinds: one is luminescent and the other is photonic. Compared with the luminescent sensors, the photonic MOFs sensors don't require any molecular level functionalization^[6]. Moreover, the signals of photonic MOFs are able to be read out directly making them more convenient. Existing reports on photonic MOFs sensors focused on thin films and periodic structures from templates that restricted the generalization of those methods^[7]. Each method is only suitable for one or certain types of MOFs. Also, using templates during the fabrications of MOFs sensors requires more processing steps, which results in complicated treatments and limits their large scale fabrication. Bottom-up routes are very promising for fabricating various structures consisting of particles. The self-assembly of particles of different sizes and shapes, including metal, polymers, metal oxides and semiconductors, has been studied recently. Based on these self-assembled structures, functions such as sensing, catalysis, and electronic applications have been developed^[8], making self-assembly increasingly attractive. Studies of self-assembly of MOFs particles are just at the beginning, and none of the existing papers have reported the applications of self-assembled MOFs.

In this chapter, a series of Zr-MOFs are controlled to be synthesized as monodispersed particles via adding modulator in the reactions (Figure 4.1). The monodispersed particles are further self-assembled into large-scale 2D and 3D superstructures. The MOFs particles showed hexagonal arrangement after packing. Self-assembled UIO-66 particles have been chosen to demonstrate the application of sensing because UIO-66 is very stable under harsh conditions when compared to the others MOFs. Though UIO-66 is a carboxylic acid-based MOF, the fabricated photonic sensors show great stability towards many chemical vapors even when exposed to NH_3 . The signal can be directly read out with the eyes because the MOFs sensors exhibit color changes in seconds. The work here demonstrates the point that self-assembled MOFs structures are of great importance for developing functional MOFs.

Figure 4.1. Schematic illustration of the synthesis and self-assembly of UIO-66 particles.

4.2 Experimental section

4.2.1 General information

We bought all the commercial reagents from Sigma-Aldrich (ACS grade) and used without further treatment unless otherwise noted. X-ray diffraction (XRD) test of samples were performed on a Bruker AXS D8 Advance diffractometer using nickel-filtered $\text{Cu K}\alpha$ radiation ($\lambda = 1.5406 \text{ \AA}$). Scanning electron microscopy (SEM) images were taken by a JEOL JSM-7600 field-emission SEM. The zeta potential measurement of UIO-66

samples was conducted on a aetasizer Nano ZS(Malvern Instruments) using water as a solvent. Thermogravimetric analyses (TGA) were recorded on a Q500 TGA (TA Instruments). Nitrogen sorption isotherms of UIO-66 dry powder were tested by Micromeritics ASAP 2020 adsorption apparatus at 77 K, 1 bar. The basic requirements for the UIO-66 powder before the measurement is activating: all the samples stay in 300 °C for 1 hours and another 20 hours at 250 °C. Through the Micromeritics ASAP 2020 built-in software by analyzing nitrogen adsorption and desorption isotherms, the final data including specific Langmuir and Brunauer-Emmett-Teller (BET) surface areas were obtained.

4.2.2 Acetic acid modulated synthesis of UiO-66.

ZrCl₄ and BDC were dissolved in 5ml DMF separately and then combined together, and then corresponding acetic acid was added in the mixture in a 30ml glass vial. In this project, metal ion and ligands molar ratio was fixed at 1 and their concentrations were modulated in a wide rage. After the fully mixed, the glass vial was capped and put into 120 °C for 24 hrs. The product was washed by 3 times with DMF after collected by centrifugation, and soaked in methanol at 60 °C for 3 times under 60 °C. At last, the product was washed in methanol for another 3 times. A point should be highlighted is that the size of UIO-66 crystal is slightly different from batch to batch.

4.2.3 Acetic acid modulated synthesis of other zirconium carboxylate MOFs.

A similar procedure was used in synthesizing other zirconium carboxylate MOFs as in UIO-66. ZrCl₄ was still used as the metal ion part and the ligand was exchanged to 2-amino-1,4-benzendicarboxylic acid (NH₂-BDC), 1,4-naphthalenedicarboxylic acid (1,4-NDC), 2,6-naphthalenedicarboxylic acid (2,6-NDC), and 4,4'-biphenyldicarboxylic acid (BPDC) correspondingly. The molar ratio between metal ion and the ligands was fixed at 1 and their concentrations were modulated in a wide range. The product was washed by 3 times with DMF after being collected by centrifugation, and soaked in methanol at 60 °C 3 times under 60 °C. At last, the product was washed in methanol for another 3 times. A

point should be highlight is the sizes of UIO-66 crystal are slightly different from batch to batch even under the same experiments conditions.

4.2.4 Surface modification of MOF crystals with PVP.

MOF crystals were collected by centrifugation and redispersed in a solution of PVP (0.375 g, $M_w = 55,000$) in 15 mL of water. The mixture was shaken with a vortex agitator for 24 hours. PVP-modified MOF crystals were collected by centrifugation and washed three times with water to remove excess free PVP.

4.2.5 2D self-assembly of MOF crystals.

Piranha solution (H_2SO_4/H_2O_2 , 70:30 (v/v)). *Caution: Piranha solution is a very strong oxidant and very dangerous for using when there is no gloves, goggles and face shielded.* treated glass slides and silicon wafers (70 °C, 50min), rinsed with DI water several times before drying under nitrogen flow. According to a previous report, the 2D self-assembly of MOFs crystals was performed on a water surface (Li, C. et al. *Chem. Mater.* **2009**, 21, 891.) The procedure was as follows: a 25mm x 25mm glass slide was set at the center of a 14 cm diameter long petri dish. The petri dish was filled with DI water carefully until the water touched the edge of the glass slide. Then about 200uL UIO-66 suspension (10 mg/mL) was dropped on the slide, the suspension spread on the water quickly at the boundary between glass slides and water. The petri dish was then fully filled with DI water, and 2-3 drop of 2% aqueous solution of sodium dodecyl sulfate (SDS) was added to consolidate the UIO-66 film. Then a close-packed monolayer formed. The monolayer was subsequently transferred onto various platforms, such as glass or silicon. The transferred film was dried under ambient conditions.

4.2.6 Photolithography template 2D MOFs pattern.

The Si (100) wafers were spin coated with a layer of photoresist (SU-8) at 4000 rpm for 60 seconds and subsequently baked at 90 °C for 3 minutes on a hot plate. Linear arrays were fabricated by photolithography using a custom-made chrome mask. Then, silica wafers with photoresist patterns were developed in a 0.4% NaOH aqueous solution for 45

seconds, washed with DI water, and dried with nitrogen flow. All the products were baked at 100 °C or 30mins. Patterned silica wafers were used as molds to fabricate polydimethylsiloxane(PDMS) mold in a 80°C oven overnight. Langmuir-Blodgett induced 2D self-assembly MOFs film was transferred onto patterned PDMS, and dried under N₂ flow. A thin film of (poly(vinyl alcohol) (5% PVA) was spin coated (1000rpm,30s) on a silicon wafer, PDMS was set on PVA thin film, and put into 100 °C oven. 1.5hrs later, PDMS was taken out and peeled from the silica wafer carefully.

4.2.7 3D self-assembly of MOF crystals.

PVP-modified MOFs were first suspended in a 15mL centrifuge tube and vertically placed on the rack for 24 hours. Then 0.5mL of suspension on the top and bottom of the tube was disposed of to obtain uniform MOFs crystals in the suspension. The rest of the product was collected by centrifugation and re-dispersed in 1.5mL DI water. The mixture was then ultrasonicated for 2 hours, and ~1.5 ml of the aqueous suspension of PVP-modified MOF crystals (~20 mg) was loaded in a glass pipette (inside diameter of 6 mm and length of 150 mm) with flame-sealed tip and vertically placed at 4 °C. After sedimentation of the MOF crystals was completed, the transparent supernatant was carefully removed and the sample was dried at room temperature. This step usually lasts several weeks long.

4.2.8 Characterization of MOFs sensors by UV-Vis spectra

Through multiple transfer process, a 5-layered UIO-66 film on a glass substrate were fabricated. After each transfer, the substrate was dried under ambient conditions. Then the glass substrates were cut into 7mm x 15mm rectangles. Before each test, the film was purged by N₂ flow thoroughly to remove guest molecules inside. A quartz cuvette with cotton on the bottom was used for holding the MOFs film. In a typical test, a small drop of organic solutions (10 uL) was absorbed by the cotton, and then the UIO-66 film was quickly put into the cuvette and sealed with Parafilm. After each test, the film need to be recovered under N₂ flow before starting a new test.

4.3 Result and discussion

4.3.1 Synthesis monodispersed MOFs crystals

Since many factors of the experiments influence the final results, both the concentration of the solution and acetic acid were varied. The results are as followed: Acetic acid was used as a modulator in the experiment to control the shape of the UIO-66 crystals. When there is no acetic acid added into the precursor, UIO-66 particles are in various sizes without regular shapes (Figure 4.2a). Once mixed with an adequate amount of acetic acid, the MOFs grow into octahedral particles^[9]. In experiments, MOFs particles appeared regular shapes by increasing acetic acid's concentration. However, when the concentration of acetic acid was higher than 4.8M, MOFs particles exist in different shapes and small MOFs particles tend to aggregate to form large particles. (Figure 4.2)

Figure 4.2. SEM images of samples synthesized with 8 mM ZrCl_4 , 8 mM BDC, and acetic acid of concentrations of a) 0, b) 0.08, c) 0.4, d) 0.8, e) 1.6, f) 4.8M, respectively. Scale bar: 100nm

According to these results, further experiments were designed in which the concentration of zirconium chloride and terephthalic acid were varied with fixed amount acetic acid added in the precursor. Before being kept inside a 120°C oven overnight, all the precursors were sieved through a 200nm filter and treated by ultrasonication to fully mix the chemicals. The concentration of acetic acid was fixed at 3M while modulating the amount of zirconium chloride and terephthalic acid. In the experiments, we set 10 groups

so that the concentrations ranged from 4mM to 25mM and one 10mM group without passing the 200nm filter as a control (Figure 4.3).

Figure 4.3. SEM images of samples synthesized with 3M acetic acid and ZrCl_4 & BDC of concentrations of a) 4, b) 5, c) 6, d) 7, e) 8, f) 9, g) 10, h) 10(control), i) 15, j) 20, k) 25mM respectively. Scale bar: a)-h) 500nm; i)-k) 375nm

With a fixed amount of acetic acid in experiments, the MOF crystals all showed a relatively uniform size and shape. Though the 25mM sample gave larger MOFs particles than others', we are not sure it was caused by the high concentrations of ZrCl_4 and BDC since the samples varied from batch to batch. In another experiment, the ration between acetic acid to ZrCl_4 &BDC were fixed at 300 while the concentrations of ZrCl_4 &BDC changed from 4mM to 15mM. MOFs crystals are uniform above 8mM of ZrCl_4 &BDC, while there are small particle present in 4mM and 5mM samples with more defects on the particles (Figure 4.4). Since acetic acid modulated synthesis was explained as the control of shapes due to acetic acid selectively binding to certain facets of the MOFs, facets

without binding to acetic acid grow faster than other facets. Finally it results into the formation of octahedrons. Compared with the results in Figure 4.1, the only difference between group 4.3A(4.3B) and 4.4A(4.4B) is the concentration of acetic acid in the precursors with their concentrations are 3M and 1.2M separately. It probably comes from the fact that acetic acid is not enough in 4.4A. When not enough acetic acid was added, not all of the MOFs crystals' corresponding facets would bind with acetic acid, some zirconium chloride and BDC will grow randomly on the surface of MOFs particles. Thus, the random growth will lead to defects on the MOFs particles, explaining the differences between these results.

Figure 4.4. SEM images of samples synthesized with fixed ratio between acetic acid and ZrCl_4 & BDC to 300, concentrations of ZrCl_4 & BDC a) 4, b) 5, c) 6, d) 7, e) 8, f) 9, g) 10, h) 15mM respectively. Scale bar: 500nm

It's important to obtain enough samples to self-assemble into 3D structures. Based on the fact that the average particle size varied from batch to batch, we could only enlarge the reaction volume if we wanted to obtain more samples with uniform size. However, when the volume exceeded 20mL, the particles are heterogeneous, distributing from several nanometers to more than 1 micrometer. These observations came from another experiment, which was mainly designed for investigating the relationship between time and particle growth (Figure 4.5).

Figure 4.5. SEM images of UIO-66 samples synthesized with 8 mM ZrCl_4 (BDC) and 2.4 M acetic acid at 120 °C for different reaction time: a) 90 minutes, b) 3 hours, c) 6 hours, and d) 10 hours. Scale bar: 100nm

Notably, after the samples have passed more than 3hrs in 120 °C, it seems that there is no dramatic change in particle shape and size. However, 60mins of reaction time is not enough for the formation of MOFs particles and the precursor is still transparent. After the samples were checked under SEM, no MOFs particles were found. When compared with 90mins particles, the particles size is quite approximate to final products though the crystals are not sharp enough.

All of the results illustrated that UIO-66 particles mainly grow during the period from 60mins to 90mins. The fact that the precursors became turbid in just 30 mins (the time between 60mins to 90 mins) supports the observation that UIO-66 grows very quickly in a short time. Nearly all of the reagents reacted to form the final products. We could obtain about same amount of MOFs powders after drying under vacuum.

Figure 4.6. SEM images of crystals of zirconium-carboxylate MOFs synthesized with ligands of a) 2-amino-1,4-benzendicarboxylic acid ($\text{NH}_2\text{-BDC}$, 8 mM ZrCl_4 , and 2.4 M acetic acid), b) 2,6-naphthalenedicarboxylic acid (2,6-NDC, 8 mM ZrCl_4 , and 1.2 M acetic acid), c) 1,4-naphthalenedicarboxylic acid (1,4-NDC, 8 mM ZrCl_4 , and 2.4 M acetic acid), and d) 4,4'-biphenyldicarboxylic acid (BPDC, 7 mM ZrCl_4 , and 1.05 M acetic acid) Scale bar: 1 μm

Another reason for the heterogeneous size distribution may be due to the fast growth process during the synthesis, where even small changes in the precursors will be enlarged under the fast process. Once there is not enough acetic acid in the precursors, the acetic acid cannot bind to all the specific surface of MOFs particles. Then, more MOFs randomly formed quickly, leading to wide size distributions.

We also synthesized other Zr-based MOFs according to the methods used for UIO-66. The conditions of these experiments are listed in Figure 4.6. Uniform UIO-66- NH_2 crystals were synthesized by modulating the concentrations of acetic acid, zirconium chloride, and $\text{NH}_2\text{-BDC}$, though a few more defects were found in UIO-66- NH_2 when compared to UIO-66. However, there are always small particles when 2,6-NDC, 1,4-NDC and BPDC were used. These small particles cannot be eliminated by simply changing chemical concentrations and ratios.

Table 4.1 To choose the most uniform UIO-66 particles for self-assembling, we measured the sizes of 50 particles for every sample and calculated the average size and standard deviation. The results are shown below:

Statistics of UIO-66 particles size under different experiment conditions					
No.(Figure)	c(ZrCl ₄ /BDC) mM	c(acetic acid) M	average particles size(nm)	standard deviation(nm)	CV(%)
4.3A	4	2.4	435.5	58.7	13.4
4.3B	5	2.4	399.8	39.5	9.8
4.3C	6	2.4	351.6	33.2	9.4
4.3D	7	2.4	414.7	35.5	8.5
4.3E	8	2.4	358.3	25.3	7.1
4.3F	9	2.4	410.3	35.3	8.6
4.3G	10	2.4	370.3	21.5	5.8
4.3H(control)	10	2.4	459.6	35.8	7.8
4.3I	15	2.4	387.7	24.5	6.3
4.3J	20	2.4	465.4	28.4	6.1
4.3K	25	2.4	883.9	55.1	6.2

From calculating results in Table 4.1, the most uniform UIO-66 samples were synthesized under 10mM ZrCl₄ and BDC with 3M acetic acid, which has the smallest standard deviation (SD) and coefficient of variation (CV). The sample was chosen as the particles for self-assembly in following experiments. Group 4.3H was designed for comparing with 4.3G to illustrating the effects of filtration. The particles size in the control group is larger than group 4.3G and is accompanied by larger SD and CV. It can be explained by the following: the precursors are more purified with less environmental influences such as dust after filtration. Filtration is helpful in the synthesis because it minimizes external influences on the reaction. According to the above results, all precursors are filtered by a 200nm filter before 120 °C reaction in oven to yield more uniform MOFs particles.

4.3.2 2D self-assembly of UIO-66

To attain a self-assembly UIO-66 structure, we chose Langmuir-Blodgett (LB) method to fabricate 2D self-assembled MOFs structures. Before the Langmuir-Blodgett experiment, the UIO-66 particles were modified by a 2.5% PVP in solution on a Vortex for 24hrs. After the modification, UIO-66 particles were washed in DI water to eliminate the excess PVP on the particles. Then, about 20mg UIO-66 particles were dispersed in 1.5mL 1:1 water/ethanol mixture before Langmuir-Blodgett experiment. A 25mm x 25mm glass slide was placed at the center of a Petri dish (14cm in diameter and 1.5cm in depth), and DI water was added into the Petri dish until it touched the edges of the glass slide. 200uL mixture was dropped on the glass slide carefully. Once the mixture contacted the bound of water and glass slide, it would spread quickly on the water surface. When the water surface was fully covered by UIO-66 particles, the Petri dish was filled by DI water slowly. After the dish was left standing for about half an hour, 1 to 2 droplets of 2% SDS solution was added into the Petri dish to make the UIO-66 pack closely (Figure 4.7 a). Then, the close-packed UIO-66 monolayer was transferred to different solid supports, such as glass slides or Si wafers.

Figure 4.7. 2D self-assembly UIO-66 film after pushed by 2% SDS on water surface (a) and transferred on a silica wafer (b).

The reflected light from the UIO-66 film on the water surface showed various colors. When observed from different angles, the film presented green, blue or light gray. Even when observed from one direction, different areas on the film showed corresponding colors (Figure 4.7). This is derived from the phenomenon called thin-film interference,

which occurs when incident light waves reflected by the upper and lower boundaries of a thin film interfere with one another to form a new wave. Thus, the thin film will show enhanced colors at some places but not others. The transferred UIO-66 film on a silica wafer presented more uniform blue reflected light. These MOF thin films could be further developed for applications in gas sensing and gas separation.

Figure 4.8. SEM images of 2D self-assembly UIO-66 thin film on silica wafer via Langmuir-Blodgett method.

Figure 4.8 showed typical SEM images of a self-assembled UIO-66 monolayer after being transferred onto a silica wafer. Though several defects were found from the image (Figure 4.8), most of the monodispersed UIO-66 crystals were ordered arranged with their 111 facets contacting the surface. And the monolayer of UIO-66 particles consisted of many small closely packed domains in which the particles were of a single orientation. The lack of long-range orientation may have resulted from the fast consolidation of the crystal upon adding the SDS. The process was too fast to be rationally controlled by us, and probably the self-assembled UIO-66 monolayer was not stable enough to resist disturbances from the great changes of surface tension. If the standard LB technique developed by the Yang et al had been used, the precisely controlled surface intension would help us obtain a better UIO-66 monolayer.

By simply repeating the transfer process, multiple-layer UIO-66 film was fabricated. The film thickness can be precisely tuned by the layer-by-layer process, and the orientations of these crystals were not diminished even the number of the layers was increased. The defects on the film also did not increase when the number of transferred processes was

increased (Figure 4.9). These observations ensure that the UIO-66 thin film can be further fabricated to devices without introducing more defects. The cross section of these self-assembly thin films supported the fact that most of the crystals contacted with silica through their 111 facets and that the thicknesses of the MOFs thin film could be controlled accurately by layer-by-layer strategy (Figure 4.9 d, f, g). The XRD results of 1, 2, and 3 layered UIO-66 thin film showed that the orientation of these crystals are in accordance with the result that 111 facets contact with the surface, as seen from the SEM images. Furthermore, with an increasing number of layers, the orientation of these crystals on the solid platform is still the same which was also supported by our results in SEM the images. (Figure 4.9)

If the thickness or the reflective index of the 2D self-assembled structure is changed, they will exhibit various colors because of the thin film interference. Three layers of self-assembled UIO-66 crystals were transferred to a silica wafer layer-by-layer with each layer shorter than the previous one, and then a silica wafer with three UIO-66 domains were developed (Figure 4.10). On the silica substrate, each layer presented a different color from green to gray, which could be further used for sensing.

Figure 4.9. SEM images of 1 layer a), 2 layers b) and 3 layers c) 2D self-assembly UIO-66 crystals and their corresponding cross sections (d,e,f).

Figure 4.10. a) 1, 2, and 3 layers UIO-66 transferred on a same silica wafer. b) XRD patterns of silicon platform-supported thin films consisting of one, two, and three layers of monolayers of microcrystals prepared by repeating the transfer process.

4.3.3 2D self-assembly based fabrication

The 2D self-assembled UIO-66 monolayer was also transferred on a polymer (PDMS) stamp for further treatment such as patterning or fabricating to potential devices. In a typical experiment, PDMS monomers were poured onto a PDMS stamp with a UIO-66 monolayer, and then polymerized in the oven. An orientated UIO-66 thin film was embedded into polymer and the structures were very stable when compared to a normal MOFs thin film. The embedded UIO-66 thin film was potentially useful for a continuous gas separation (Figure 4.11).

Figure 4.11. a) UIO-66 monolayer was embedded into polymer. b) The basic procedure for fabricating 20μm wide UIO-66 lines. Orange triangles represent UIO-66 crystals, gray parts represent PVA layer and large blue polygons represent PDMS stamp. c) SEM images of 20μm UIO-66 lines patterned via micro-contact printing and its high magnification image of line edge d).

We also used micro-contact printing (μCp) to further pattern the 2D self-assembled UIO-66 monolayer. The procedure of fabricating PDMS stamp with 20μm wide lines was mentioned in the experimental section above. Then the stamp was treated with plasma before transferring LB film on it. The basic procedure is listed in Figure 4.11 b as a scheme. After being transferred, the UIO-66 thin film was dried under a mildly N_2 flow. Then, the stamp was placed on the top of a silica wafer whose surface was spin coated by a thin layer of polyvinyl alcohol (PVA). It was put into a 100°C oven for 1.5hrs in order to polymerize PVA with UIO-66, and then the stamp was peeled off carefully from silicon wafer. The 20μm wide lines consist of UIO-66 crystals formed on the silicon wafer. The 2D self-assembled UIO-66 structures were robust, able to be further fabricated to desired pattern or devices. More work can be done in this field when combined with lithography techniques or other kinds of materials.

4.3.4 Self-assembled MOFs sensors

The fabrication of a MOFs sensor was achieved by repeating the above mentioned self-assembly with LB. Glass substrates were chosen here as supporting materials. In Figure 4.12 a, we are able to observe the color change of self-assembled MOFs films from different viewing angles. The colors of MOFs sensors are derived from the ordered 3D arrangement of UIO-66 crystals. Further characterization of MOFs sensors was conducted by UV-Vis spectra. Firstly, UIO-66 sensors with different number of layers was fabricated by LB. All the four samples consist of same sized monodispersed UIO-66 crystals. As we can see from Figure 4.12 b, as the number of layers increases, the absorbance peak becomes stronger and sharper. The results here were in accordance with former studies of photonic structures made of silica particles. The advantage of the process described here, however, is that more sensitive sensors could be fabricated by repeating the transfer process. The position of peaks are determined by the size of MOFs crystals. By choosing the proper crystal size, we are able to design photonic sensors with peaks in certain positions. We demonstrated this point by fabricating two MOFs sensors with different UIO-66 crystals. In Figure 4.12 c, sensors consisting of larger crystals show a red-shift peak with other parameters fixed. Under some circumstances, the guest molecules have their own absorbing peak in the visible range, and so choosing proper crystals will avoid the overlapping of peaks. The UIO-66 films could also be transferred onto Si wafer. And the absorbance properties are characterized by UV-Vis spectra. However, the sensors based on Si exhibited multiple peaks which was unsuitable for sensing (Figure 4.12d). Increasing the layers of films will bring even more peaks than single layer structures. Thus, glass is a better candidate for supporting the self-assembled MOFs crystals.

Figure 4.12 a) the self-assembled films exhibit pink and light green when viewed from different angles. b) UV-Vis absorbance curves of self-assembled UIO-66 films of different layers. c) Self-assembled films which were built by different size UIO-66 crystals show absorbance peaks at different wavelength. d) Reflection spectra of UIO-66 crystals films.

A five-layered self-assembled film constructed with UIO-66 crystals was used here to demonstrate the performance of MOFs photonic sensors. The MOFs sensor was exposed to several common solvents including water, ethanol, toluene, etc. UV-Vis spectra of UIO-66 crystals film are shown in Figure 4.13a where an obvious peak shift was observed. However, the UIO-66 sensor showed a larger peak shift when exposed to toluene, DMF, chloroform, ethanol, methanol and acetone compared to water under ambient conditions. This was attributed to the interactions between guest molecules and UIO-66 crystals. The mechanism of UIO-66 sensors is based on the Bragg equation. When UIO-66 sensors absorb guest molecules, the reflective index of the entire system would change because of the adsorption of guest molecules. Generally, the more guest

molecules absorbed by the sensors, the larger shift will appear on UV-Vis spectrum. And molecules having a high affinity with UIO-66 will also result in larger shifts. The large differences before and after the exposure to chemical vapors can be directly seen with naked eyes due to the color changes, especially for DMF and ethanol. Since MOFs are quite designable, it is possible to design suitable MOFs for sensing. For example, selective MOFs sensors could be designed by choosing MOFs crystals with small aperture size. These sensors will block molecules with sizes larger than the aperture from entering the MOFs crystals which would further result in fewer changes of reflective index. Another advantage of photonic MOFs sensors is high stability towards corrosive chemicals. As we known, UIO-66 was built from carboxylic acid ligands and hence would decompose in alkaline solutions quickly. However, sensing via vapor phase will make sure the UIO-66 crystals remain stable. Thus, operating the MOFs sensors under a vapor phase will extend the range of molecules than can be detected. When exposed to 1% aqueous ammonia vapor, the UIO-66 sensor showed a 16nm peak shift on UV-Vis spectrum. Compared with its fast decomposition in alkaline liquid, the sensor was quite stable under vapor phase. Moreover, the peak shifts are also reliable and quick.

4.4 Conclusion

In this chapter, monodispersed Zr-based MOFs crystals were synthesized by modulator route. The precise tailoring of the starting concentration of both Zr^{4+} and BDC is also important for achieving the final monodispersed crystals. Then, the monodispersed UIO-66 crystals were chosen as the building block of superstructures. 2D and 3D MOFs superstructures are fabricated by the LB and sedimentation method, respectively. In the 3D superstructures, UIO-66 crystals exhibited hexagonal arrangement over hundreds of micrometers. To demonstrate our statement that self-assembled MOFs will show unique, structure-derived properties, we fabricated a photonic sensor with monodispersed UIO-66 crystals. The signal of these sensors could be directly read out by naked eye. The results are also promising considering the short responses time, stable recyclability and selectivity towards various vapors. The fabrication route also represents a general and convenient way to make MOFs devices.

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Chapter 5

Hierarchical Hollow CuS Polyhedrons Originated From Metal-organic Frameworks and Application in Lithium-ion Battery

In this chapter, MOFs with regular shapes were synthesized by adding modulators during the synthesis. Then MOFs crystals were transferred into corresponding metal sulfide hollow particles. When evaluated as electrode materials in lithium-ion battery, they exhibited enhanced properties.

5.1 Introduction

Metal-organic frameworks (MOFs), also known as porous coordination polymers (PCPs), and generated by the self-assembly of metal ions/clusters and organic ligands, are a kind of crystalline material with high surface area and nearly infinite structural possibilities^[1]. As a result of their unique properties, MOFs have emerged as promising candidates in plenty of research fields, such as gas storage/separation^[2], catalysis^[3], sensing^[4], drug delivery,^[5] and even water treatment^[6]. Importantly, colloidal-sized MOFs with regulated, uniform shapes are garnering increasing research attentions in recent years^[7]. Thus, much effort has been devoted to the synthesis of MOFs with controllable crystal sizes, shapes and compositions by diverse routes, especially via coordination modulation (e.g., adding carboxylic acid^[8] or polymer^[9]). Up until now, plenty of anisotropic MOF particles ranging from cubes to octahedrons have been achieved.

Owing to the hybrid nature of MOFs originated from both inorganic and organic components, they have also been employed recently as the qualified matrix and templates for the preparation of porous nanostructured oxides^[10], carbon^[11] and polymers^[12]. For example, using MOFs as templates, Lin and co-workers synthesized hollow silica rods with variable shell thicknesses^[12], and Xu et al. fabricated porous carbon with exceptionally high surface area up to 2872 m² g⁻¹^[14]. Moreover, highly complex multiple ball-in-ball metal oxides and shaped polymer nanoparticles were also obtained. Generally speaking^[12-13], these MOF-derived materials have distinct advantages of larger specific surface area and higher degree of porosity compared to other methods, and thus could play a crucial role in functional applications. In particular, MOF-derived hollow structures have attracted great interests in the field of lithium-ion batteries (LIBs)^[14]. This is because the highly porous shell and the large internal void space can ensure efficient electrolyte penetration, offer a large electrode-electrolyte interface, and buffer the significant volumetric expansion and contraction induced by lithium uptakes and removals^[15]. Up to date, several studies in the literature have reported on the formation of hollow metal oxides derived from MOFs as LIB electrodes^[16], nevertheless, the fabrication of metal sulfide from MOFs and their applications as electrode materials for LIBs is still at an early stage.

Metal sulfides (e.g., CuS and CoS) with unique physical and chemical properties (e.g., higher electrical conductivity as well as mechanical and thermal stability than those of their corresponding metal oxides) which also have rich redox chemistry that contributes to a high specific capacity (several times higher than those of carbon/graphite-based materials) make themselves stand out from other LIB electrode materials^[17]. Unfortunately, in addition to the volume change, the lithiation of metal sulfides is accompanied by the formation of insulating polysulfide Li_2S_x ($2 < x < 8$) intermediates that readily dissolve in organic electrolytes, leading to capacity degradation^[18]. Moreover, CuS electrodes were verified to undergo both displacement and conversion reactions during the charge/discharge process, which made it more complicated together with Li_2S_x dissolving^[19]. Fortunately, a very recent report on CuS nanosheets exhibited a high capacity of 642 mAh g^{-1} at the 270th cycle, indicating that unique nanostructure could enhance the performance of metal sulfides tremendously for LIB applications^[20].

The basic synthetic strategy is illustrated in Figure 5.1. Firstly, cubic and octahedral HKUST-1 crystals were synthesized by a modulator route. Different kinds of modulators were added into the reaction to achieve cubic or octahedral crystals correspondingly. Then these HKUST-1 crystals were transferred into CuS hollow particles under low solvothermal temperature. After eliminating the rest of the ligands in the reaction solutions by washing the as-prepared samples with ethanol 3 times, the achieved CuS hollow particles were used as electrodes materials in lithium-ion batteries. The hollow CuS particles exhibited enhanced capacity and high stability in the battery tests. Also, to demonstrate this method as a general route, a Co-based MOF: ZIF-67 was synthesized and then transferred to CoS hollow particles through the same route. Here we reported the controlled synthesis of MOFs via modulating and developing a general and facial route for porous, hollow metal sulfides. This would be important for the further applications of hollow, porous metal sulfides in many fields.

Figure 5.1. Schematic illustration of the synthesis of cubic and octahedral HKUST-1 particles. The HKUST-1 particles are further transferred to their corresponding hollow CuS particles.

5.2 Experimental section

5.2.1 General information

All chemicals were purchased from Sigma-Aldrich and used as received. X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance diffractometer (Cu $K\alpha$ radiation, $\lambda = 1.5406 \text{ \AA}$). Scanning electron microscope (SEM) images were acquired by using a JEOL JSM-7600 field-emission SEM. Transmission electron microscope images were taken under a JEOL JEM-2100F microscope with a 200kV accelerating voltage. Nitrogen adsorption isotherms of powder samples were measured with a Micromeritics ASAP 2020 adsorption apparatus at 77 K up to 1 bar. Before measurement, each powder sample was degassed by heating under vacuum at 393K for 24hrs unless other noted. Further analysis of Brunauer-Emmett-Teller (BET)

and specific Langmuir surface area, pore size, and pore volume was conducted on the built-in software from ASAP. Thermogravimetric analyses were performed on a Q500 TGA (TA Instruments).

5.2.2 Synthesis of octahedral HKUST-1 particles

43.49mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 37.8mg Benzene-1,3,5-tricarboxylic acid (BTC) were dissolved in 10mL ethylene glycol (EG). Then 0.5g PVP ($M_w \sim 55000$) was added and sonicated for 60 mins to afford a homogeneous solution. Subsequently, the mixture was transferred into a glass vial and placed into an electric oven presented at 120 °C for 12hrs. Finally, the blue powder was collected by centrifugation and washed with ethanol.

5.2.3 Synthesis of cubic HKUST-1 particles

41mg $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ and 2.5g lauric acid were dissolved in 10mL butanol after sonicating for 20mins. Then, 20mg BTC was added into the mixed solution. After the BTC was fully dissolved, the mixture was transferred into an autoclave. The autoclave was put into an electric oven at 140 °C for 3hrs. The blue powder was collected by centrifugation and washed with ethanol 3 times.

5.2.4 Synthesis hollow CuS particles

The as-prepared HKUST-1 particles (one batch of cubic particles or half batch of octahedral particles) were redispersed in 5mL ethanol and 5mL 0.1M thioacetamide (TAA) was added into the HKUST-1 suspension. The mixture was sonicated for 5mins to make a well-dispersed suspension. Then the suspension was added into a glass vial and put into an oven at 90 °C for 1hr. After the reaction, the products were carefully collected by centrifugation and washed with ethanol 3 times at a low centrifugation speed.

5.2.5 Synthesis of hollow CoS particles

10mg ZIF-67 synthesized according to existing methods was dispersed in 5mL ethanol. Then 5mL 0.1M TAA was added into the ZIF-67 suspension. The mixture was sonicated for 5mins and transferred into an oven at 90 °C for 1hr. After the reaction, the products were collected by centrifugation and washed with ethanol.

5.2.6 Electrochemical measurement

The coin-type cells were assembled in an argon-filled glove box, where both moisture and oxygen levels were less than 1 ppm. The working electrodes were fabricated by mixing of CuS, carbon nanotubes and poly(vinylidene fluoride) (PVDF) at a weight ratio of 70:20:10 in N-methylpyrrolidone (NMP) and then pasting on the copper foils. The lithium foils were used as counter/reference electrodes and the electrolyte was a solution of 1M LiPF₆ in ethylene carbonate (EC)/dimethyl carbonate (DMC) (1/1, w/w). The cells were tested on a NEWARE multi-channel battery test system with galvanostatic charge and discharge in the voltage range of 0.005-3.0 V.

5.3 Result and Discussion

5.3.1 Synthesis of cubic and octahedral HKUST-1 crystals

As mentioned in the introduction, adding modulators into a synthetic reaction of MOFs was one of the most common methods for the controlled synthesis of MOFs over size, shapes and even functions. Also, adding modulator was more convenient since there is no further requirement of precise equipments. The realm of modulators is also abundant, which provides researchers with nearly infinite choices for achieving the final targets.

The synthesis of octahedral HKUST-1 crystals was achieved by using polyvinylpyrrolidone (PVP, MW~55000) as a modulator. Polymers are well known modulators in the synthesis of MOFs. In Figure 5.2, the SEM images showed HKUST-1 crystals synthesized by adding different amount of PVP in the precursors. From Figure 5.2 a, we found that there were two types of crystals in the image: small, octahedral particles and large, spindle-like particles. This was because of the small amount of PVP added; as a result, not all of the HKUST-1 nuclei were bonded with enough PVP. Having PVP taking participate into the growth, the crystals grew slower but along certain directions. Those nuclei without enough PVP bonding tended to grow faster and not that regular in shape. When the amount of PVP was increased in the precursor, octahedral HKUST-1 particles were synthesized (Figure 5.2b). Further increasing the amount of PVP added did not lead to better crystals because the modulators would slow down the growth speed of nuclei. This would lead to rather ill-defined crystals (Figure 5.2c).

Adding too much PVP into the precursor will result in low yield since excess modulator suppresses the growth heavily. In Figure 5.2d, only spherical-like particles were synthesized due to the large amount of PVP added.

Figure 5.2. SEM images of HKUST-1 particles when different amount PVP a) 0.2g, b) 0.5g, c) 1g, d) 2g were added into precursors.

The cubic HKUST-1 crystals were synthesized by using lauric acid as modulator^[21]. The synthesized cubic HKUST-1 was shown in Figure 5.3. As can be observed from the field emission scanning electron microscope (FESEM) images, well-defined cubes were successfully obtained from the solvothermal reaction through the modulation of lauric acid. In the higher magnification SEM images, HKUST-1 crystals showed very smooth surfaces, indicating the well crystalline nature of them. Also the crystals here are well defined.

Figure 5.3. SEM images of cubic (a,b) and octahedral (c,d) HKUST-1 particles synthesized with lauric acid and PVP as modulators, respectively.

From the TEM images, we found that the contrasts of the HKUST-1 particles are homogenous, demonstrating their dense and uniform nature of the HKUST-1 particles (Figure 5.4). Powder X-ray diffraction (PXRD) results further confirmed the crystalline structure of the HKUST-1 particles (Figure 5.5a). The PXRD pattern matches well with the standard patterns, indicating no impurities in the product. The Brunauer-Emmett-Teller (BET) surface area of the HKUST-1 synthesized in ethylene glycol (EG) was approximately $1099 \text{ m}^2 \text{ g}^{-1}$, as obtained from the nitrogen adsorption-desorption analysis (Figure 5.5b). The thermogravimetric analysis (TGA) result was also in accordance with previous publication: the first weight drop zone which below 200°C is ascribed to the loss of solvent and coordinated guest molecules inside HUKST-1 channels and the second weight loss zone which above 350°C was caused by the decomposition of organic ligands (Figure 5.5c).

Figure 5.4. TEM images of a), b) cubic and c), d) octahedral HKUST-1 particles.

Figure 5.5. a) XRD patterns of simulated, cubic and octahedral HKUST-1. b) Nitrogen adsorption-desorption isotherm for HKUST-1 particles at 77 K up to 1 bar. c) Thermogravimetric analysis (TGA) of HKUST-1 particles in N_2 .

5.3.2 Transformation of HKUST-1 to CuS

Hollow CuS particles were synthesized from HKUST-1 which acted as both the templates and the copper ion precursor, and thioacetamide (TAA) as the sulfur precursor. Before transferring the as-synthesized HKUST-1 particles to CuS particles, HKUST-1 particles were washed in ethanol several times to eliminate the modulators and other unreacted chemicals. Then the HKUST-1 suspension was poured into 0.05 M TAA ethanolic solutions. To ensure a uniform HKUST-1 suspension, the mixture was ultrasonicated for 10 mins before the reaction. Finally, the suspension was kept in an oven at 90 °C for 1 hour, after which the products were collected by centrifugation at a speed of 3000 rpm. The morphology of the obtained particles were well maintained (Figure 5.6a-b), and we can see the surfaces of these particles became rough and were composed of smaller particles. Interestingly, under TEM, the particles were found to be hollow with porous shells (Figure 5.6c-d).

Figure 5.6 SEM (a,b), TEM (c,d) and HRTEM (e) images of cubic and octahedral CuS particles. (f) XRD patterns of standard and synthesized CuS samples.

Figure 5.7. a) high resolution TEM (HRTEM) image of hollow CuS. b) selected area electron diffraction (SAED) pattern of the CuS shell. c) TGA of hollow CuS particles in O_2 . d) Nitrogen adsorption-desorption isotherm for hollow CuS particles at 77 K up to 1 bar.

The high resolution TEM (HRTEM) images are displayed in Figure 5.5e. The PXRD spectrum of the products was consistent with standard CuS PXRD patterns (Figure 5.6f). In accordance with the PXRD result, Figure 5.7a depicted a lattice spacing of 0.3 nm corresponding to (102) plane of CuS. The selected area electron diffraction (SAED) pattern of the shell proved the polycrystalline nature of the CuS hollow particles (Figure 5.7b). TGA analysis of CuS hollow particles under O_2 showed approximately 20% weight loss, which can be mainly attributed to the transformation of CuS to CuO (Figure 5.7c). When the hollow CuS particles with porous shell were evaluated for the BET surface area, they exhibited a moderate value of $47.87\text{ m}^2\text{ g}^{-1}$ (Figure 5.6d).

Figure 5.8. a) SEM image of HKUST-1/CuS particle which shows the particle has a HKUST-1 core and a CuS shell b) XRD pattern of CoS hollow particles derived from ZIF-67.

The formation mechanism of CuS particles was similar to several previous reports^[21-22]. At the beginning of the reaction, S^{2-} anions hydrolyzed from TAA reacted with Cu^{2+} cations dissolved from the surface of the HKUST-1 templates, resulting in a thin layer of CuS on the surface of HKUST-1. As the reaction continued, a greater proportion of the HKUST-1 template was consumed to form more CuS on the surface and as a result, the void space between HKUST-1 and CuS shell widened (Figure 5.8a). At the end, all of the HKUST-1 was transferred to CuS, giving rise to unique hollow structured CuS particles. To address the generalization of our above-mentioned method, we also expanded our method to another imidazole based MOFs, ZIF-67 (Figure 5.9a-b), which was successfully transferred to CoS hollow particles under similar conditions. Figure 5.9c-d show the CoS hollow particles with a 40nm thick shell consisting of small particles similar to that of CuS. The PXRD pattern (Figure 5.8b) of the hollow CoS particles illustrated that the products are amorphous.

Figure 5.9. TEM images of a), b) ZIF-67 particles and c), d) CoS hollow particles.

5.3.3 Performance in lithium-ion batteries

It is worth noting that hierarchical hollow particles are actively pursued for application in LIBs due to such unique structures' capability of accommodating the large volume change during the charge/discharge process, leading to improved capacity and cycling performance. As an important electrode material, CuS has been studied for a long time. Nevertheless, the poor stability of CuS limits its use for rechargeable batteries. Most of the CuS suffered enormous loss of capacity after a few cycles^[23]. Here, the hollow CuS boxes are tested as the anode materials for LIBs and showed much higher capacity and stability up to 50 cycles. Figure 5.10a displays the charge/discharge profiles of CuS boxes at 1st, 2nd and 50th cycles. The two plateaus at about 2.05V and 1.6V were attributed to the formation of Li_xCuS and Cu respectively, fitting well with previous

studies (Figure 5.10a)^[24]. The CuS boxes exhibited an ultrahigh initial discharge capacity of 1233 mA h g^{-1} with a capacity retention of 784 mA h g^{-1} at the 2nd discharge. The formation of solid electrolyte interface (SEI) was the main reason for the large capacity loss (36%) in the first cycle. Though one third of the initial capacity was lost at the first cycle, the CuS boxes kept its excellent cycling stability up to 50 cycles (Figure 5.10b).

Figure 5.10. Charge and discharge profiles of cubic CuS particles at 100 mA g^{-1} . (b) Cycling performance and Coulombic efficiency of cubic CuS particles at the same current density.

In addition, the CuS boxes exhibited a high Columbic efficiency around 95% from the 5th cycle onwards. At 50th cycle, the CuS boxes achieved a capacity of 836 mA h g^{-1} , which was even higher than the second cycle. This capacity gain with increasing cycle number can be explained as the activation process of the fresh CuS with the possible formation of reversible polymeric surface layer^[20, 24]. Notably, the activation process

finished within 30 cycles, which was faster compared to those of metal sulfide nanomaterials reported previously^[20, 24]. And the faster activation process indicated that the porous nature allowed the CuS reacted more easily with Li^+ . To further investigate the rate performance of CuS boxes, we tested the CuS boxes under different current densities (Figure 5.11). The test was started at a rate of 300 mA g^{-1} , and a capacity of about 480 mA h g^{-1} was achieved. Followed by the higher current densities of 500 mA g^{-1} , 1000 mA g^{-1} , 2000 mA g^{-1} , 3000 mA g^{-1} , the capacities of 420 mA h g^{-1} , 320 mA h g^{-1} , 260 mA h g^{-1} , and 200 mA h g^{-1} were achieved respectively. When the current density was switched back to 300 mA g^{-1} , the capacity was able to return back to a level of 450 mA h g^{-1} , which is almost the same as the starting value. This result indicates the high stability and good reversibility of the hollow CuS boxes.

Figure 5.11. Rate performance at various current rates ranging from 300 mA g^{-1} to 3000 mA g^{-1} .

To the best of our knowledge, both the capacity and cycling stability of the hollow CuS boxes in this work are superior compared to existing reports on nanostructured CuS. Sphere-like CuS particles processed an initial capacity of $\sim 600 \text{ mA h g}^{-1}$ and just after 10 cycles, the capacity dropped to 100 mA h g^{-1} .^[24] Cu monoliths showed an increase in capacity from 1st cycle to 100th cycle, with its corresponding capacity of $185.1 \text{ mA h g}^{-1}$

and 468.3 mAh g⁻¹[24]. Furthermore, the CuS nanosheets exhibited an ultrastable capacity of 642 mAh g⁻¹ at the 270th cycle but with a low capacity of 321 mAh g⁻¹ at the 20th cycle[24]. According to previous studies, the unique nanostructures of CuS are probably the main reason relating to their remarkable properties in LIBs. In particular, the porous shell will promote the diffusion of Li⁺ ions which is also in step with the faster activation process of CuS boxes[24]. The hierarchical structure with hollow interiors is able to buffer the volume variation during the electrochemical reactions[16]. Furthermore, the subunit of the CuS shells is quite small (down to around 10nm), which is favorable for CuS to take part in the electrochemical reactions.

5.4 Summary

In summary, cubic and octahedral HKUST-1 MOFs were synthesized successfully under the modulation of lauric acid or PVP respectively by solvothermal routes. A facile and general route to transfer the MOFs to their corresponding metal sulfides has been demonstrated. The obtained metal sulfides exhibited unique hollow structures with porous shells. When the CuS cubes were evaluated as electrode materials for LIBs, high capacity and cycling stability were achieved due to the unique nanostructures of CuS. Considering the enormous kinds of MOFs, this strategy provides a novel strategy of preparing hollow structured metal sulfides in a facile way. And the corresponding metal sulfides are able to be used over a broad range of applications with enhanced performance.

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Chapter 6

A template-free route towards fabricating mesoporous and yolk/shell MOFs and NPs@MOFs with enhanced selective catalytic properties

A template free strategy of synthesis mesoporous and yolk-shell MOFs crystals is developed here. Control on reaction time will lead to different products. The integrated shells after solvothermal treatment are proved by their selectivity in catalysis.

6.1 Introduction

Endowed with the unique properties of high porosity and flexible tunability, metal-organic frameworks (MOFs) have recently and quickly gained popularity in the fields of gas storage/separation^[1], catalysis, sensors^[2], drug delivery^[3] and batteries^[4]. In particular, the rigid and uniform pores inside MOFs act as molecular sieve in selective catalysis^[5]. Furthermore, MOFs can also act as a matrix to hosting guest catalysts, increasing their stabilities^[5a, 6]. As a result, both the MOFs themselves and guest catalysts which are encapsulated in those MOFs are studied for their enhanced performance. However, most of the MOFs possess micropores which will severely limit the diffusion rate of reactants and thus lead to a low catalytic activity. Since mesoporous MOFs are able to conquer the problems mentioned above, diverse routes are developed to create mesoporous MOFs^[7]. One typical strategy is using enlarged metal clusters and ligands to synthesize mesoporous MOFs^[8]. Although this method resulted in designable MOFs with more uniform pore sizes, the mesopores were mostly small based on the fact that larger ligands and metal clusters will result in unstable structures and even interpenetration. The complicated synthesis of larger ligands also restricted the generalization of this method. Even for the synthesized mesoporous MOFs, supercritical drying technique was required for removing guest molecules inside MOFs in case the frameworks collapsed^[8b]. Template synthesis of mesoporous MOFs is another popular method since it is convenient to operate and provide us with hierarchical pore distributions^[9]. Mesopores inside MOFs contribute to higher diffusion rates with high surface area maintained by the micropores^[9b]. The pore size was also controllable when different surfactants were used. Obviously, removing templates from the as-prepared mesoporous MOFs will lead to the collapse of structures. And mesoporous MOFs synthesized through this route are probably mechanical mixtures of micropores and mesoporous MOFs.

Yolk-shell structures are a new type of core-shell structures which exhibit enhanced properties in catalysis, drug delivery and the energy sciences due to unique core@void@shell structures^[10]. Compared to traditional core-shell structures, the yolk-shell structures not only can prevent the cores from aggregating but also provide more active sites of the core in addition to a homogenous nanoreactor in the void space. Thus yolk-shell structures are more welcomed based on the above reasons. However, only a few yolk-shell structured MOFs were reported very recently^[11]. A template method was introduced by Tsung's group, where Cu₂O layers on the Pd nanoparticles (NPs) were used as sacrificial templates after embedding the Pd@Cu₂O into ZIF-8. After the Cu₂O was selectively dissolved, a yolk-shell structured Pd@void@ZIF-8 was obtained. Wang et al. developed a method for the synthesis of hollow MOFs. After introducing PVP-modified NPs into the reaction, yolk-shell NPs@MOFs were achieved^[12]. The disadvantages from existing methods are obvious in that the template method usually requires more steps in the synthesis,

which lead to more complex synthesis. In another method, not all of the hollow MOFs were able to encapsulate the NPs.

With standing on the limitations mentioned above, we developed a template-free route to synthesize both mesoporous and yolk-shell MOFs. Mesoporous or yolk-shelled MOFs are able to be synthesized by the same route. Shorter reaction times would result in formation of mesoporous MOFs while extending reaction time would generate yolk-shell structured MOFs.

Figure 6.1 Synthetic strategy for the meso-MOFs or yolk-shell MOFs heterostructures.

6.2 Experimental section

6.2.1 Synthesis of monodispersed UIO-66

ZrCl₄ and BDC were dissolved in 10mL DMF separately and then combined together. The final concentration of ZrCl₄ and BDC were 0.008M. Then acetic acid was added in the mixture in a 30mL glass vial. The combined mixtures were placed into an ultrasonic bath for 20min to obtain a homogeneous solution. After the solution was fully mixed, the glass vial was capped and put into 120 °C for 24 hours. Product was washed 3 times with DMF after collected by centrifugation, and soaked in ethanol at 60 °C 3 times under 60 °C. Finally, the product was washed in ethanol for another 3 times and soaked into the ethanol

6.2.2 Synthesis of monodispersed UIO-66NH₂

ZrCl₄ and BDC-NH₂ were dissolved in 10mL DMF separately and then combined together. The final concentration of ZrCl₄ and BDC-NH₂ were 0.008M. Then acetic acid was added in the mixture in a 30mL glass vial. The combined mixtures were placed into an ultrasonic bath for 20min to get a homogeneous solution. After the solutions was fully mixed, the glass vial was capped and put into 120 °C for 24 hours. Product was washed 3 times with DMF after collected

by centrifugation, and soaked in ethanol at 60 °C 3 times under 60 °C. At last, the product was washed in ethanol for another 3 times and soaked into the ethanol.

6.2.3 Preparation of mesoporous or yolk-shell UIO-66/UIO-66-NH₂

The synthesized UIO-66 or UIO-66-NH₂ crystals were soaked into 10mL ethanol in an autoclave. Before heating, the suspension was ultrasonicated for 10 mins to achieve a homogeneous mixture. The autoclaves were taken out at different times. The samples were collected by centrifugation and further washed by ethanol for 6 times.

6.2.4 General information

All chemicals were purchased from Sigma-Aldrich and used as received. X-ray diffraction (XRD) patterns were obtained using a Bruker AXS D8 Advance diffractometer (Cu K α radiation, λ = 1.5406 Å). Scanning electron microscope (SEM) images were acquired by with a JEOL JSM-7600 field-emission SEM. Transmission electron microscope images were taken under the JEOL JEM-2100F microscopes with an 200kV accelerating voltage. Nitrogen adsorption isotherms of powder samples were measured with a Micromeritics ASAP 2020 adsorption apparatus at 77 K up to 1 bar. Before each measurement, each powder sample was degassed by heating under vacuum at 393K for 24hrs unless other noted. Further analysis of Brunauer-Emmett-Teller (BET) and specific Langmuir surface area, pore size, and pore volume was conducted on the built-in software from ASAP. Thermogravimetric analyses were performed on a Q500 TGA (TA Instruments).

6.2.5 Synthesis of Pt nanoparticles with PVP capped on the surfaces

133mg PVP (MW~29,000) was added into 180mL methanol, then 20mL 6.0 mM H₂PtCl₆ aqueous was further added into the PVP solution, after which the mixture was heated to its boiling point in air for 3hrs. Then methanol was removed with a rotary evaporator. The remaining Pt NPs were collected by precipitation after being mixed with acetone and centrifugation. All of the NPs were washed with a mixture of chloroform and hexane for removing excess PVP. The final product was dried under vacuum and then redispersed into DMF.

6.2.6 Synthesis of Pt@UIO-66

10ml 8mM DMF solution of ZrCl_4 and 10ml 8mM DMF solution of benzenedicarboxylic acid (BDC) was mixed together and 2.4ml acetic acid and 0.4 ml Pt NPs solutions were added into the mixture subsequently. Then the whole reaction precursors were put into an ultrasonic bath for 20mins. Then the mixture was put into a 120 °C for 24hrs. The products were washed by DMF for 3 times and another 3 times of ethanol. The as-synthesized product was soaked into ethanol under 60 °C to help the exchanging of DMF molecules to ethanol. At last, the product was soaked into ethanol for further use.

6.2.7 Catalytic characterization of Pt@meso-UIO-66 and yolk/shell Pt- ZrO_2 @UIO-66

Hydrogenation of olefins (cis-cyclooctene, trans-stilbene, triphenylethylene or 1,1,2,2-Tetraphenylethylene) was carried out in ethyl acetate solution in a static hydrogen atmosphere (1 bar). In a typical experiment, the catalyst (0.01g) was loaded in a reactor and the residual air in the reactor was expelled by flushing hydrogen several times. Ethyl acetate (3 mL) was added in the reactor and the mixture was ultrasonicated for 10 min to afford a homogeneous suspension. Olefin (0.1 mL) was then added in the reactor and the mixture was sonicated again for 10 min. After the reactor was again flushed one more time with hydrogen, the reaction was allowed to proceed at 1 atm of hydrogen and 35 °C for 24 h. After the reaction, the catalyst powder was filtered off and the filtrate (n-hexene and cis-cyclooctene) was analyzed using a gas chromatograph (Agilent, 6890N) equipped with a HP-5 column (Agilent) and FID. It is worth noting that the commercial chemical of 95% cis-cyclooctene (Aldrich, Cat No. 125482) contains ~3.6% cyclooctane as detected by the gas chromatograph analysis. In addition, trans-stilbene, triphenylethylene and 1,1,2,2-Tetraphenylethylene was analyzed using NMR spectrometer (Bruker AV400 (400MHZ)).

Table 6.1. The concentration of reactants.

Reactant	Concentration ($\text{mol}\cdot\text{L}^{-1}$)
cis-cyclooctene	0.12 (0.05 mL)
trans-stilbene	0.08 (40 mg)
triphenylethylene	0.05 (30 mg)
tetraphenylethylene	0.03 (20 mg)

6.3 Result and discussion

6.3.1 Mesoporous and yolk/shell UIO-66/UIO-66-NH₂

With the former mentioned problems in current synthesis of mesoporous MOFs and yolk-shell structured NPs@MOFs, here we developed a template-free method, which circumvented all the abovementioned difficulties. No templates were required during the synthesis. The basic idea was illustrated in Figure 6.1, most MOFs would decompose under certain elevated temperature. If we were able to control the decomposition process and slow down the decomposition, targeted MOFs would be synthesized during this method. From figure 6.2 and figure 6.3, we found the octahedral structures of UIO-66-NH₂ will last till 16hrs under solvothermal condition of ethanol. Only a few crystals with broken shell showed the yolk-shell structures and most of the crystals still hold stable octahedral shells. From the SEM images of the solvothermal treated UIO-66-NH₂ crystals, we conjectured the decomposition first happened inside the crystals. Because most of SEM images of UIO-66-NH₂ showed these crystals easily maintained their shapes and no differences were found till 12hrs (Figure 6.3a). Even after long time treatment (16 hrs), the shells were still able to sustain the original octahedral shapes. Through the broken shelled UIO-66-NH₂ crystal, a small octahedra exhibit inside the shell. Furthermore, from SEM images, the shell of all the crystals with different reaction times were still as smooth as the starting crystals. It indicated the shell should be well maintained. The well protected shells could be further used as molecular sieves. We will discuss this point in the catalytic part.

Figure 6.2. SEM images of UIO-66-NH₂ crystals after a), b) 4hrs and c), d) 8hrs solvothermal treatment in ethanol solutions.

Figure 6.3 SEM images of UiO-66-NH₂ crystals after a), b) 12hrs and c), d) 16hrs solvothermal treatment in ethanol solutions.

To further investigate our hypothesis, TEM was used to characterize the samples. In Figure 6.4 and Figure 6.5, UiO-66-NH₂ crystals after solvothermal treatment for different times were shown. At the beginning, crystals didn't show any changes under TEM. The uniform contrast of images proved that little changes happened at 2hrs (Figure 6.4a and 6.4d). Then, with an reaction time of 3hrs, the crystals start to collapse from the center. From high magnification TEM image (Figure 6.4e), lots of tiny holes appeared at this time. The contrast of the crystals in low magnification TEM image (Figure 6.4b) was still not sharp. With increasing the reaction time to 4hrs, pores inside UiO-66-NH₂ crystals became larger. From Figure 6.4f, we found the pores' size were mainly ranged in mesoscale. And compared 4hrs samples (Figure 6.4c) with 3hrs samples (Figure 6.4b), the sharper contrast of the center part indicated the formation of more and larger pores in

these crystals. Through the fine control of the decomposition process of UIO-66-NH₂, mesoporous UIO-66-NH₂ crystals were synthesized.

Figure 6.4 TEM images of UIO-66-NH₂ crystals after solvothermal treatment for a), d) 2hrs; b), e) 3hrs; c), f) 4hrs.

Further increasing the reaction time, more and more inside parts of UIO-66-NH₂ collapsed (Figure 6.5). At a reaction time of 8hrs, a large void space formed inside UIO-66-NH₂ crystals (Figure 6.5 a and 6.5d). The diameter of the void space is estimated about half the size of the whole crystal. And some dark aggregates formed in this stage. In the TEM images, the dark aggregates didn't have certain shapes. With another 4hrs reaction time, most of dark aggregates tended to grow and move together and a single core appeared. However, the cores here still didn't possess any regular shapes (Figure 6.5b and 6.5d). The void space was larger than last stage that means more UIO-66-NH₂ decomposed. Till to 16hrs reaction time, the core inside UIO-66-NH₂ formed an octahedral shape, the same to the crystal itself (Figure 6.5c and 6.5f). At the same time, the shells of UIO-66-NH₂ became thinner. According to the TEM images, the thickness of the shells is estimated around 30nm. And the materials of the cores are postulated that it should be ZrO₂ since there was no additional element introduced into the reaction and ZrO₂ is a very stable metal oxide under high temperature. Further evidences will be provided in reaction mechanism

part. Based on above results, UIO-66-NH₂ crystals were easily transferred to mesoporous UIO-66-NH₂ and yolk-shell structured ZrO₂@Void@UIO-66-NH₂ (YS-Z@V@U) crystals.

Figure 6.5 TEM images of UIO-66-NH₂ crystals after solvothermal treatment for a), d) 8hrs; b), e) 12hrs; e), f) 16hrs.

From the SEM and TEM results, we found the shells of these crystals were very stable even after 16hrs solvothermal treatment. Very few broken shells would appear after 16hrs reaction. And for the rest samples, no broken shells were found. To verify whether the shells maintained the structure of UIO-66-NH₂, XRD were used to characterize all the samples (Figure 6.6). Compared with UIO-66-NH₂ crystals, the XRD didn't show changes even for the 16hrs sample. Though the cores were predicted should be ZrO₂, the shells were UIO-66-NH₂. Under the XRD, the intensity of UIO-66-NH₂ is much higher than the ZrO₂. It is the reason why from the XRD patterns, 16hrs still kept the same pattern as original UIO-66-NH₂. The ZrO₂ core will be proved in the discussion of reaction mechanism part later. The stability of all UIO-66-NH₂, mesoporous UIO-66-NH₂ and YS-Z@V@U were further tested by TGA. The weight loss curve showed the same trend for all three samples (Figure 6.6b). The pure UIO-66-NH₂ sample exhibited the largest weight loss since UIO-66-NH₂ hold most amount of solvent in it. The differences generated mainly from the temperature under 100°C. From 100°C to 300°C, the three samples showed

parallel curves. The weight loss below 100°C was mainly from the loss of solvent inside UiO-66-NH₂. Since mesoporous UiO-66-NH₂ already had some mesopores inside UiO-66-NH₂, these pores were no more able to trap small solvent molecules in it. The total amount of mesoporous UiO-66-NH₂ absorbed was fewer than original UiO-66-NH₂. On the TGA curves, it would result in the less weight loss under 100°C. The same also happened to ZrO₂@void@UiO-66-NH₂, but it would show the least weight loss in all three samples. With increasing the reaction time, more UiO-66-NH₂ of the crystals was transferred into ZrO₂ and less solvent molecules would be able to be trapped. The TGA results are in accord with the structures. From Figure 4.6b, we also found the fact that the solvothermal treatment didn't change the stability of unreacted part of UiO-66-NH₂. Even for the shells of ZrO₂@void@UiO-66-NH₂, it still showed the same stability after heat treatment. It will bring us a better functionalized MOFs without any decays in stability.

Figure 6.6 a) XRD patterns of UiO-66-NH₂ powders after solvothermal treatment for different time. b) Thermogravimetric analysis(TGA) of UiO-66-NH₂, mesoporous UiO-66-NH₂ and yolk-shell ZrO₂@void@UiO-66-NH₂.

The analysis of pores sizes and distributions in mesoporous UiO-66-NH₂ and YS-Z@V@U are essential for better understanding these structures. From TEM images we are only able to estimate the pore sizes. Here, Brunauer-Emmett-Teller (BET) was operated to help us further investigate the pores structures in these samples. The black isotherm represent UiO-66-NH₂ (Figure 6.7a), it showed the typical microporous solid materials isotherm. The isotherm of mesoporous UiO-66-NH₂ featured a hysteresis loop, which was generated by the mesoporous structures. And the pink isotherm exhibited combination properties of microporous and macroporous materials (Figure 6.7a). The micropores were located in the shell while the macropores mainly from the void space

between ZrO_2 and shells. The Nitrogen adsorption-desorption isotherm here further proved the shells of 16hrs samples had microporous structures, which probably were able to act as molecular level sieves. Pore size distribution results are shown in Figure 6.7b, there are two peaks on the curve, one is around 3nm and another is around 6nm. Though the pores sizes are located in mesoscale, these pores still are small. One advantage of the small mesopores is that it will not only provide enough space for molecules diffusion but also generate larger surface areas than larger mesopores. This nature will do contribution to catalysis reactions. For the YS-Z@V@U crystals, there was no sharp peak on the curve. Only a small peak around 3nm was found and the rest pores' sizes distributed evenly in mesoscale (Figure 6.7b). The Nitrogen adsorption-desorption isotherm help us further understand the pores size distribution inside all three samples and we are able to utilize these crystals in a better way.

Figure 6.7 a) Nitrogen adsorption-desorption isotherm for UiO-66-NH₂, mesoporous UiO-66-NH₂ and ZrO₂@void@UiO-66-NH₂ at 77 K up to 1 bar. b) Pore size distribution of mesoporous UiO-66-NH₂ and ZrO₂@void@UiO-66-NH₂ according to the Nitrogen adsorption-desorption isotherm.

6.3.2 Investigation of formation mechanism

According to abovementioned results, the investigation of formation mechanism behind mesoporous UiO-66-NH₂ and YS-Z@V@U crystals are important for us to better control the reaction. The unusual phenomenon of the reaction is that the decomposition happened from the center part of UiO-66-NH₂ crystals. Since for each crystal, the reaction conditions are the same and in hundreds nanometers would't change a lot. We supposed that center part of UiO-66-NH₂

was less stable than the outside part. To prove the hypothesis, an etching experiment was specially designed for the cores of UIO-66-NH₂. Firstly, the cores were synthesized when we stopped the growth at the beginning stage of UIO-66-NH₂. Then followed the same steps to wash out all the unreacted chemicals and then put the cores into a solvothermal treatment for 4hrs. For the normal UIO-66-NH₂ crystals, 4hrs treatment would result into mesoporous structures. However, the cores started to decompose at the edge part instead of from the center. In Figure 6.8a, we didn't find out any pores in the center as the 4hrs samples of UIO-66-NH₂ crystals. And when from the high resolution TEM image (Figure 6.8c and 6.8d), we found very clear crystal lattice not belong to UIO-66-NH₂. The lattice space was measured to be 0.292nm which corresponding to the (101) lattice spacing of ZrO₂. The results here prove the hypothesis the starting point of decomposition was in the center result from the differences of stabilities between cores and out layers in UIO-66-NH₂ crystals.

Figure 6.8 TEM images of UIO-66-NH₂ cores after 4hrs solvothermal treatment.

The materials of cores after the reaction were confirmed by XRD (Figure 6.9). The pure UIO-66-NH₂ cores showed a typical pattern-the sharp peaks below 10°. With increasing the reaction time,

the peaks below 10° became weaker and broader which represented more UIO-66-NH₂ was consumed. At a reaction time of 3hrs, a peak appeared at 30° while the most strong peaks of UIO-66-NH₂ disappeared after 8hrs which indicated the totally decomposition of UIO-66-NH₂. At last, one more peak at 50° appeared which also belong to ZrO₂. The XRD patterns of UIO-66-NH₂ cores after different time treatment also matched the results of normal UIO-66-NH₂ crystals. At 8hrs, the cores inside UIO-66-NH₂ were all decomposed and a shell left. Increasing reaction time to 16hrs, the ZrO₂ was able to form a better crystalline structures and all the rest ZrO₂ aggregates to an octahedral cores.

Figure 6.9 XRD patterns of UIO-66-NH₂ cores before and after solvothermal treatment for different times.

6.3.3 Enhanced performance in selective catalysis

Through a simple solvothermal process, we synthesized both mesoporous UIO-66-NH₂ and YS-Z@V@U crystals. The larger pores inside these crystals would provide faster diffusion routes than in microporous crystals. Here we chose Pt@UIO-66 crystals acted as catalyst to prove the enhanced property of mesoporous and yolk-shell structured crystals. And at the same time, expanding the current system to another kind of MOFs will shed light on the generalization of this strategy. The synthesis of Pt@UIO-66 crystals came from our former works. And following the same strategy of UIO-66-NH₂, Pt@mesoporous UIO-66 and Pt/ZrO₂@void@UIO-66 crystals were successfully synthesized (Figure 6.10 and Figure 6.11).

Figure 6.10 TEM images of Pt@mesoporous UIO-66 crystals.

Figure 6.11 TEM images of Pt/ZrO₂@void@UIO-66 crystals.

In Figure 6.10, the Pt nanoparticles still stayed inside UIO-66 crystals and the similar mesopores generated after 3hrs treatment in ethanol. It's important that the Pt nanoparticles didn't aggregate which thanks to the confinement effect of the UIO-66. For the Pt@UIO-66 crystals, the UIO-66 would firstly grow around Pt nanoparticles and immobilize Pt nanoparticles. From the higher magnification TEM image (Figure 6.10d), we further made sure Pt nanoparticles kept separately. Since aggregation of nanoparticles will result in severely loss in activity, maintaining the Pt

nanoparticles from aggregation was essential for following catalytic reactions. For the yolk-shell Pt/ZrO₂@void@UIO-66 crystals, all the crystals possessed octahedral ZrO₂ cores and UIO-66 shells (Figure 6.11a). The thickness of shells here was estimated around 30nm (Figure 6.11b). No leakages happened based on the fact that there were no small particles sticking on shells (Figure 6.11b). On a higher magnification TEM image (Figure 6.11c), the white arrow showed the location of Pt nanoparticles. During the reaction, Pt nanoparticles still located in the center part of ZrO₂. However, whether the ZrO₂ octahedral cores were densely packed or not was unknown. If the Pt/ZrO₂@void@UIO-66 crystals are able to exhibit activity in the following catalysis, the ZrO₂ cores will not be densely packed since the molecules outside will diffuse into the active Pt nanoparticles.

The catalytic activities of Pt@UIO-66, Pt@mesoporous UIO-66 and Pt/ZrO₂@void@UIO-66 crystals for the hydrogenation of olefins of different sizes are shown in Figure 6.12. The control group showed no catalytic activity toward trans-stilbene, triphenylethylene and tetraphenylethylene since the sizes of these reactants are larger than the aperture size of UIO-66 crystals. The rigid pore structures blocked large molecules but allow small molecules pass through their pores to contact with the active Pt. nanoparticles. For the cis-cyclooctene, the conversion rate is 4.59% for 24hrs. Compared with UIO-66 crystals, the mesoporous exhibited a much higher conversion rate of 23.91%, 4 times higher. Mesoporous solved the disadvantage of normal microporous MOFs in the catalysis: though the regular pores of MOFs provide the selectivity in reactions but also bring the problem of slow diffusion rate of the reactants. The Pt/ZrO₂@void@UIO-66 had a conversion rate of 6.63% for the cis-cyclooctene, 44% higher than Pt@UIO-66. The conversion rate was not as high as Pt@mesoporous UIO-66, it should be ascribed to the ZrO₂. Though the ZrO₂ cores were not densely packed, the diffusion inside the ZrO₂ is more difficult for the cis-cyclooctene based on the results. No activities toward the other three olefins proved the integrated shells after the solvothermal reaction. The large void space between ZrO₂ cores and UIO-66 shells are suitable platforms for other functional particles. Though for the catalytic reactions are not as good as mesoporous structures, other functions could be investigated in future for yolk-shell structured MOFs.

Figure 6.12 Catalytic activity of Pt@UIO-66, Pt@mesoporous UIO-66 and Pt/ZrO₂@void@UIO-66 in the hydrogenation of cis-cyclooctene, trans-stilbene, triphenylethylene and tetraphenylethylene.

6.4 Conclusion

In this chapter, we developed a simple template-free strategy toward fabricating mesoporous and yolk-shell structured UIO-66/UIO-66-NH₂ crystals. The formation mechanism was proved. After the solvothermal treatment, both the mesoporous and yolk-shell structured UIO-66/UIO-66 NH₂ maintained their integrated layers. A series of hydrogenation reactions were chosen to both illustrate the enhanced properties and the intact shells' structures of mesoporous and yolk-shell structured Pt@UIO-66. The new strategy not only provided a convenient way for the post-synthetic treatment but also open a new world of studies of mesoporous and yolk-shell MOFs.

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Chapter 7

Future works

In this chapter, proposed future works based on current results are presented. They are extensional projects of self-assembly of MOFs and other functional particles. 4 projects are discussed in this chapter.

7.1 Self-assembly of NPs@MOFs crystals

We developed a strategy of encapsulation functional nanoparticles into MOFs before in our

group^[1]. Nearly all kinds of functional materials could be introduced into MOFs during the synthesis. Self-assembly is a powerful tool for fabricating functional materials with novel structures. The combination of self-assembly techniques with NPs@MOFs will generate more novel functions which not belong to neither of them separately. For example, a self-assembled bulk NPs@MOFs monolith is a better platform than the randomly packed MOFs monolith since the diffusion routes in the random one probably will be blocked while the self-assembled one provide a predictable route. Another application of self-assembled NPs@MOFs probably should be in the photonic devices. The self-assembled UIO-66 could be used as sensors for detecting chemical vapors. And based on the large reflective index differences between MOFs and metal nanoparticles plus the controllable distributions of nanoparticles inside MOFs, more complex photonic devices could be fabricated.

The preliminary results in Figure 7.1 showed the difficulties in the preparation of monodispersed NPs@MOFs crystals. Because the introduction of NPs at the beginning of the growth of MOFs will also infect the process and make it hard to fine control the growth of monodispersed crystals. According to our formed experiences, choosing a suitable modulator is essential for controlling the growth. And other parameters such as concentrations of reactants, temperature and reaction volumes will also make an effect on the final results. More works should be done in the future.

Figure 7.1 TEM images of 1wt% Pt NPs@UIO-66 crystals.

7.2 Self-assembly of MOFs crystals with other materials

Self-assembly of MOFs crystals with other materials will provide us with novel functions or make a great enhancement of existing properties. For example, if we self-assembly the MOFs

crystals with graphene oxide(GO) sheets on water surfaces via LB, we probably will get a continuous film. And since the mechanical strength of GO sheets are much strong than MOFs and GO sheets themselves are great binders for other materials^[2]. If a freestanding thin film of GO and MOFs are fabricated through this route, it will help the real applications of MOFs film in gas separation and other devices.

Figure 7.2. Dried GO/PEDOT:PSS gel makes a sticky adhesive for (a) PET ribbon and (b) glass slides. (c) A vial of 20 mL of GO in water can be supported by a platform glued together by the gel. (d) Shear stress-strain curves of two PET stripes glued together by GO/PEDOT gel (blue) and PEDOT:PSS (red), respectively. The inset shows the geometry of measurement.

Another choice is self-assembly of MOFs crystals with metal NPs. Metal NPs showed great properties in many fields. However, the stability of metal NPs are very important for keep the functions. Once aggregation happened, most of the metal NPs will lose their activities. Though encapsulation these metal NPs into MOFs is a good strategy for enhancing their stability, some metal NPs will decompose or aggregate during the synthesis which make it's not that general for all metal NPs. Thanks to the mild conditions for self-assembly process, the aggregation can hardly happened during self-assembly. If the metal NPs self-assembly with MOFs crystals together, they will be confined in certain locations in the bulk self-assembled superlattice. During reactions such as catalysis, the immobilized NPs wouldn't move to anywhere unless the whole superlattice collapsed.

In the sensing area, the MOFs crystals around NPs will also help absorb certain kinds of molecules and increasing the concentration of target molecules in the nearby environment. It will probably give a better detection limit than bare NPs.

7.3 Synthesis mesoporous and yolk-shell MOFs through vapor phase route

In chapter 6 we reported a template-free route for the synthesis of mesoporous and yolk-shell structured MOFs. Though it's convenient and didn't require any template during the reactions, large amount of solvent are still needed for the reactions. All the organic solvents are harmful to our environment. To improve this strategy, vapor phase reaction is a better choice than solvothermal route. Nearly zero waste will generate by this route since a little amount of solvent is needed for the reaction.

Figure 7.3. (a) Schematic drawings illustrating the steaming process to create perforated GO. First, GO monolayers were deposited on substrates by Langmuir-Blodgett technique. Then, the substrates were suspended above deionized water in the sealed vessel, and heated at 200 C. (b and c) AFM images showing the same GO sheet before and after being steamed for 10 h, respectively. Pores and cracks can be clearly seen after steaming. (d) Height profiles along the white line in b and c. All scale bars = 2 μm .

An existing example for vapor phase decomposition of GO was reported^[3], through a simple vapor phase etching at an elevated temperature(Figure 7.3). The products showed holes with a size from several nanometers to tens of nanometers. The etched GO can be used as good sensor for chemicals. We believe through fine-tuning the reaction conditions and choose the suitable solvent we should make mesoporous and yolk-shell MOFs similar with in chapter 6 by this route.

7.4 Investigating jamming effect of MOFs crystals

Jamming of colloidal particles is a very interesting phenomenon and the understanding of the jamming mechanism is essential for many research areas. In fact, jamming happened often in our daily life: the traffic jam. In food industry, the ketchup and ice cream also utilize the jamming effects. Even for the shower gel, jamming exists in it. The jamming effects existed nearly everywhere, and investigating the jamming effects for MOFs crystals will bring us more new functional MOFs.

Usually the temperature, volume concentration and forces are three main parameters for controlling the jamming state (Figure 7.4)^[4]. And sometimes jamming effect will help us trap unusual structure state and fabricating novel structures. The conditions of self-assembly process and jamming appeared are similar, if we are able to get the jammed MOF, it will show great applications in many field.

Figure 7.4. The jammed region, near the origin, is enclosed by the depicted surface. The line in the temperature-load plane is speculative, and indicates how the yield stress might vary for jammed systems in which there is thermal motion.

Firstly, the jamming effect will help us make unusual structures of self-assembled MOFs. For example, MOFs particles formed spherical-like wall on the interface between oil and water. However, if we want other shapes such as ribbons and non-spherical shapes, the normal self-assembly on water/oil interface can't make it. By utilizing the jamming effect, researchers are able to make different self-assembled structures on the interface^[5].

Secondly, since the jammed state usually formed in a confined space and strong interactions between the basic particles. These forces are not only to support the surface tension in liquid but also will make these structures stronger than common self-assembled structures^[6]. This is an alternative way for making stable self-assembled structures and no surface modifications on the based particles are required.

Thirdly, based on the formation parameters of jammed particles, we can develop smart materials that could respond to certain conditions. For example, if we can create a jammed state MOFs crystals on interface. The jammed state will only allow small molecules pass through the interface while when we elevate the temperature the jammed state disappeared; all molecules are able to pass through the interface. By control the temperature, we create a small molecular gate.

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List of Publications

Dongrong Xiao¶, **Chenlong Cui**¶, Weina Zhang, Yayuan Liu, Fengwei Huo* (Co first author) A template-free route towards fabricating mesoporous and yolk/shell MOFs and NPs@MOFs with enhanced selective catalytic performance Under preparation

Chenlong Cui, Xianhong Rui, Yayuan liu, Weina Zhang, Chencheng Sun, Dongrong Xiao, Ping Cui, Qingyu Yan* and Fengwei Huo* Synthesis of Hierarchical Hollow CuS Polyhedrons Originated From Metal-organic Frameworks and Application in Lithium-ion Battery Submitted

Chenlong Cui, Yayuan Liu, Hongbo Xu, Shaozhou Li, Weina Zhang, Ping Cui and Fengwei Huo* Self-assembled metal-organic frameworks crystals for chemical vapor sensing *Small*, 2014, 10, 3672.

Weina Zhang, Yayuan Liu, Guang Lu, Yong Wang, Shaozhou Li, **Chenlong Cui**, Jin Wu, Zhiling Xu, Danbi Tian, Wei Huang, Joseph S DuCheneu, W David Wei, Hongyu Chen, Yanhui Yang, Fengwei Huo* Mesoporous Metal - Organic Frameworks with Size - , Shape - , and Space - Distribution - Controlled Pore Structure *Advanced Materials*, 2015, 18, 2923.

Weina Zhang, Guang Lu, **Chenlong Cui**, Yayuan Liu, Shaozhou Li, Wenjin Yan, Chong Xing, Yonggui Robin Chi, Yanhui Yang, Fengwei Huo* A Family of Metal-Organic Frameworks Exhibiting Size-Selective Catalysis with Encapsulated Noble-Metal Nanoparticles *Advanced Materials*, 2014, 24, 4056.

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