Metal Ions and Nanoparticles Embedded into

Surface-Mounted Metal Organic Frameworks

Zur Erlangung des akademischen Grades eines

DOKTORS DER NATURWISSENSCHAFTEN

(Dr. rer. nat.)

Fakultät für Chemie und Biowissenschaften

Karlsruher Institut für Technologie (KIT) – Universitätsbereich

genehmigte

DISSERTATION

von

M. Sc. Wei Guo

aus

Huangshi, Hubei, P. R. China

Dekan: Prof. Dr. Willem Klopper

Referent: Prof. Dr. Christof Wöll

Korreferent: Prof. Dr. Stefan Bräse

Tag der mündlichen Prüfung: 09.02.2016

I declare hereby, that this PhD thesis is based on my work and knowledge and not used other sources, references and resources mentioned in the body of this thesis.

Wei Guo

Karlsruhe, 07.01.2016

Contents

AŁ	ostra	ct		I
1	Inti	rod	uction	1
	1.1	Me	tal organic frameworks (MOFs)	1
	1.1.1		Design of MOFs	2
	1.1.	2	Synthesis methods of MOFs	3
	1.1.	3	Typical MOFs	4
	1.1.	4	Application of MOFs	5
	1.2	MC	OF thin films: preparation and applications	6
	1.2.	1	Preparation method of MOF thin films	6
	1.2.	2	Application of MOF thin films	12
	1.3	Sur	face-mounted metal-organic frameworks (SURMOFs)	17
	1.3.	1	Substrate	18
	1.3.	2	Methods	
	1.4	Me	tal ions and NPs embedded into MOFs	23
	1.4.	1	Metal ions embedded into MOFs	23
	1.4.	2	Metal NPs embedded into MOFs	24
	1.5	Loa	iding metal ions and NPs into SURMOFs	26
2	Cha	arad	terization methods	28
	2.1	X-r	ay diffraction	28
	2.1.	1	Theoretical background	28
	2.1.	2	Estimation of X-ray diffraction intensity	29
	2.1.3		X-ray diffraction of the MOF thin film	31
	2.2	Infi	rared spectroscopy	32
	2.2.	1	Theoretical background	32
	2.2.	2	Transmission infrared spectroscopy	34
	2.2.3		Infrared reflection-absorption spectroscopy	34
	2.2.4		Attenuated total reflection	
	2.3	Rar	nan spectroscopy	
	2.4	Ult	raviolet–visible spectroscopy	
	2.5	X-r	ay photoelectron spectroscopy	40

2	2.6	Electrospray Ionization Mass Spectrometry	41
2	2.7	Inductively coupled plasma atomic emission spectroscopy	42
2	2.8	Time-of-flight secondary ion mass spectrometry	43
2	2.9	Scanning electron microscope	14
2	2.10	Atomic force microscopy	45
2	2.11	Transmission electron microscopy	46
2	2.12	Quartz crystal microbalance	48
2	2.13	Electrochemistry at semiconductor electrodes	49
3	Ma	terials and theoretical analysis5	51
3	1	Materials	51
	21	1 Substrates	51
	2.1	2 Chemicals	51
	J.1.		, ,
3	8.2	SAM preparation on Au substrates	52
3	8.3	Surface treatment of other substrates	53
3	8.4	Theoretical analysis	54
4	Loa	ding metal ions into SURMOFs by using benzene ring as	
nu	cleat	tion centers	56
4	.1	Loading of La ²⁷ ionic compounds into HKUST-1 SURMOFs	56 - C
	4.1.	1 Background	<u> </u>
	4.1.	2 Preparation of the La(OIf) ₃ @HKUSI-1 SURMOF)/
	4.1.	3 Results and discussion	58
	4.1.	4 Conclusions	58
4	.2	Bi ₂ O ₃ nanoparticles encapsulated into HKUST-1 SURMOF6	58
	4.2.	1 Background	58
	4.2.	2 Preparation of the Bi ₂ O ₃ @HKUST-1 SURMOF	70
	4.2.	3 Photolysis of the Bi(Ph)₃ precursor	70
	4.2.	4 Results and discussion	73
	4.2.	5 Conclusions	39
5	دما	ding metal ions into SURMOEs by using side chain of ligands as	
nu	cleat	tion centers	90

5	5.1 Loading of metal ions into functionalized SURMOF with sulfur and alkene						
si	side-chains						
	5.1.1	Background	90				
5.1.2		Preparation of the Cu ₂ (atBDC) ₂ (dabco) SURMOF	91				
	5.1.3	8 Results and discussion	92				
	5.1.4	Conclusions	98				
6	6 Loading metal ions into SURMOFs by using open metal sites as						
nu	cleati	ion centers	. 100				
6	.1	Au(CO)Cl gas-phase loading into HKUST-1 SURMOF	100				
	6.1.1	Background	100				
	6.1.2	Preparation of the Au(CO)Cl@HKUST-1 SURMOF	101				
	6.1.3	8 Results and discussion	102				
	6.1.4	Conclusions	112				
7	Con	clusions	113				
List	List of abbreviations115						
References117							
Publications							
Acl	Acknowledgments127						

Abstract

My thesis focuses on metal and metal oxide clusters embedded in surface-mounted metal organic frameworks (SURMOFs). Metal organic framework (MOF) thin films were grown on functionalized substrates using liquid phase epitaxy (LPE) process, thus forming SURMOFs. LPE technique can well control the thickness (normally in nanometer range) of the MOF thin film when a layer-by-layer growth method is used. Loading of metal ions, clusters, or nanoparticles (NPs) inside the SURMOFs does not only change the crystal structure of the host material but also modifies its properties. Choosing appropriate nucleation sites in the MOFs is a crucial step and directly influences the interaction and reaction of the loaded metal–precursor species.

The first strategy was to load metal-precursor from the solution, e.g., triphenylbismuth, into the pores of HKUST-1. In this method, the metal ions entered and were adsorbed on the phenyl ring of the ligands. However, the crucial factors were temperature, concentration, metal species, and solvent. A thorough theoretical calculation using classical force-field-based simulations analysis was performed to determine the possible number and position of metal species in the MOF. The results were found to be in full agreement with the experimental results. This structure was first stabilized by the pronounced dispersive interaction between La³⁺ or Bi³⁺ ions and the phenyl ring of the ligand. Then, the metal precursors in MOFs can be decomposed to form cluster or small NPs within the MOF network. Therefore, MOFs are an excellent template to limit the particle growth and impede the agglomeration process.

The second approach was to utilize a functionalized ligand to increase the number of nucleation centers. The functionalized ligand does not change the crystal structure of the host materials, but improves their adsorption ability for metal ions. Ligand functionalized with sulfur and alkene side-chain were investigated and used to prepare a pillar-layer SURMOF [Cu₂(atBDC)₂(dabco)]. The results reveal that the sulfur- and alkene- functionalized side-chains improved the adsorption ability of metal clusters, but simultaneously hinder the diffusion of the precursor molecules.

The last approach is to use open coordination sites (OCSs) at the metal center as nucleation center. Among the MOFs, those with OCSs at the metal center exhibit effective adsorption of small organic molecules. A metal complex with small organic molecules is required to effectively link the metal ion with the OCSs. In this study, volatile metal-organic precursors, such as [Au(CO)CI], were loaded into an open MOF framework containing OCS sites, namely HKUST-1.

Zusammenfassung

Diese Arbeit fokussiert auf die Herstellung von Metall- und Metalloxidischen Cluster sowie Nanopartikeln in Metallorganischen Gerüstmaterialien (SURMOFs). Dünne MOF Schichten können auf funktionalisierten Substraten aufgewachsen werden durch den Prozess der Flüssigphasenepitaxie (LPE). Die LPE-Technik kann auch die Dicke (in der Regel im Nanometerbereich) des MOF Films mittels Verwendung eines Schicht-für-Schicht-Wachstumsverfahren steuern. Durch die Beladung von Metallionen, Cluster oder Nanopartikel der SURMOFs wird nicht nur die Kristallstruktur des Wirtsmaterials (SURMOF) verändert, sondern auch die Eigenschaft solcher NP@SURMOF Filme. Die gezielte Verwendung aktiver Stellen in der metallorganischen Gerüstverbindungen (MOFs) ist wichtig, da die Beladung sowie die Anzahl und Art der molekularen Precursoren gesteuert werden kann.

Eine erste nützliche Strategie zum Beladen von Metall-Precursoren, ist Phenyl-Liganden als aktive Stellen zu verwenden. Bei diesem Verfahren werden die Metallionen an der Phenylgruppe des Liganden adsorbiert. Dies ist jedoch ein stochastischer Prozess und die Haupteinflußfaktoren der Methode sind Temperatur, Konzentration sowie das verwendete Lösungsmittel. Theoretische Berechnungen mit klassischen Kraftfeld Rechnungen auf Basis von Monte Carlo Simulationen wurden auf der Grundlage der möglichen Anzahl sowie der Lage der Metallspezies im MOF durchgeführt. Die theoretischen Ergebnisse konnten in guter Übereinstimmung mit experimentellen Ergebnisse gefunden werden. Diese Struktur wird zum einen durch die ausgeprägte dispersive Wechselwirkung zwischen den La³⁺- und Bi³⁺-lonen sowie dem Phenylring des Liganden stabilisiert. Anschliessend, können die beladenen Metall-Precursoren zersetzt werden, wobei sich kleine Cluster oder Nanopartikel (NPs) bilden. MOFs sind daher ausgezeichnete Template, um das Partikelwachstum zu steuern sowie die Agglomeration der hergestellten Cluster/Partikel zu verhindern.

Bei einem zweiten Ansatz wurden funktionalisierte MOF-Liganden verwendet, um die aktive Stellen in MOFs zu erhöhen. Die verwendeten funktionalisierte MOF-Liganden ändern nicht die Kristallstruktur des Wirtsmaterialien (SURMOF), verbessern aber die Adsorptionsfähigkeit für Metallionen. In dieser Arbeit wurden funktionalisierte MOF-Liganden mit aktiven Schwefel und Alken-Seitenketten untersucht. Weiterhin wurde dadurch ein Pilliard (Säule-Schicht) SURMOF [Cu₂(atBDC)₂(dabco)] aufgebaut. Die Ergebnisse zeigen, dass Schwefel und Alken-Seitenkette in MOF-Liganden die Adsorptionsfähigkeit für Metallionen/cluster erhöhen aber zugleich die Diffusion erschweren.

Bei dem letzten Ansatz handelt es sich um die Verwendung der offenen Koordinationsstellen (OCSs) an den Metallzentren im MOF-Gitter als aktive Stelle zur

Anbindung von Precursoren. Unter vielen MOF-Strukturen konnte aufgezeigt werden, dass kleine organische Moleküle mit OCSs wechselwirken oder adsorbiert werden. Um freien Metallionen oder Metal-Precursoren effektiv mit OCSs zu verknüpfen, wird ein Metall-Komplex mit niedermolekularen organischen Verbindungen aufgebaut. Hierbei beluden wir aus der Gasphase das leichtflüchtige Molekül [Au(CO)Cl] in den SURMOFs welcher an die freien OCSs des HKUST-1 SURMOFs anbindet.

1 Introduction

1.1 Metal organic frameworks (MOFs)

Inorganic porous materials, including those formed by metals and metal foams,^[1] metal oxides,^[2] porous carbons,^[3] metal organic frameworks^[4] and zeolites,^[5] have attracted increasing attention because of their flexible pore sizes and large loading capacities for guest species. These materials are also used in catalysis,^[6] chemical sensors,^[7] and gas separations.^[8] Inorganic porous materials can generally be classified into three types according to pore size: microporous (<2 nm), mesoporous (from 2 nm to 50 nm), and macroporous (>50 nm) materials.

Among the inorganic porous materials, metal organic frameworks (MOFs) have emerged as an extensive class of crystalline materials with ordered and nanoscale topography.^[9, 10] More than 20,000 MOF structures, such as HKUST-1, MOF-5, and ZIF-8, have been designed and synthesized since the first MOF material was reported in 1959.^[11] These crystalline and nanoporous MOF materials are formed by mixing two essential building blocks, namely, metal ions (inorganic units) and organic ligands (Fig. 1.1). An MOF is a crystalline coordination network of metal ions and organic ligands containing nanometer-sized cavities. The metal ions and organic ligands first form a unit cell crystal nucleus, and finally this unit cell rapidly grows by repeating coordination entities extending to chains (1D), layers (2D), and three-dimensional (3D) structures.^[12-14] This kind of material is widely applied in catalysis,^[15] gas storage,^[16] gas separations^[17] and chemical sensors.^[7]



Figure 1.1 Components and structure of metal organic frameworks (MOFs): a general scheme illustrating the coordination of metal nodes and organic ligands to a MOFs.

1.1.1 Design of MOFs

MOF material structure achieves strong plasticity and flexibility when various components (metal ions and organic ligands) are selected and assembled.

A total of 131 secondary building units (SBUs), such as triangle and rectangular (paddle-wheel) (see Fig. 1.2), have been introduced since the first metal atom was used as SBUs for the frameworks.^{[18] [19] [20]} The SBUs share one or more central oxide ions and can bridge up to two, three, or more organic ligands that directly affect the structure of MOFs. For example, the paddle-wheel Cu(OAc)₂ SBUs include two copper atoms and connect with four organic ligands to form a face-centered cubic lattice structure (e.g., HKUST-1^[21]). By contrast, the Zn₄O SBUs can bridge up to six organic ligands to form a cubic lattice structure (e.g., MOF-5^[14]). However, choosing different kinds of metal SBUs can directly influence the performance of MOFs. For example, Co(OAc)₂ and Cu(OAc)₂ SBUs have shown the same paddle-wheel structure inside MOFs [e.g., Co₂(BDC)₂(dabco)^[22] and Cu₂(BDC)₂(dabco)^[23]], but the catalytic activity of the former is much higher than the latter one.



Figure 1.2 Structural representations of several SBUs, including (a) triangle, (b) rectangular (paddle-wheel), (c) tetrahedron, (d) square pyramid, (e) rigonal prism and (f) ctahedra (Figure taken from Ref.^[20]*).*

The second design point is choosing and assembling various organic ligands (Fig. 1.3). We can obtain different pore sizes and shapes of MOFs by adjusting the length of ligands using the same SBUs (e.g., Zn_4O) (Fig. 1.3 up).^[24] Moreover, different properties can be obtained by choosing and assembling different functional linkers

(Fig. 1.3 down). The ligands with special function groups will not change the crystal structure of host materials, but will improve the interaction with guest molecules for high loading capacity.^[25]



Figure 1.3 Structure of IRMOFs and their ligands (Figure taken from Ref.^[26]).

1.1.2 Synthesis methods of MOFs

Numerous synthesis methods, such as solvothermal,^[27, 28] ultrasonic,^[29, 30] microwave synthesis,^[31, 32] electrochemical synthesis^[33] and mechanochemical synthesis.^[34, 35] have been developed to prepare MOFs. Solvothermal synthesis is the most commonly used technique, because the self-assembly reaction between metal ions and organic ligands easily occur in liquid phase.

Temperature is the most important factor for the synthesis of MOFs. Thus, the synthetic methods can be divided into several categories using different heating modes: room temperature synthesis, conventional electric heating, microwave heating, electrochemistry, mechanochemistry, and ultrasonic method (Fig. 1.4).^[36] Various MOFs with different structures (such as size, shape, and crystallinity) could be obtained by controlling and selecting the reaction temperatures. For example, HKUST-1 particles with sizes between 0.1 and 40 μ m can be obtained by controlling the temperature from 25 °C to 120 °C.^[37] In addition to temperature, many other

factors, such as solvent,^[38, 39] concentration of reactants,^[40] pH value,^[41] heating time,^[42] heating and cooling rates^[43] should also be carefully adjusted to optimize the crystallization reaction.



Figure 1.4 Overview of synthesis methods, possible reaction temperatures, and final reaction products in MOF synthesis (Figure taken from Ref.^[36]).

1.1.3 Typical MOFs

In this section, we introduce a few typical MOFs, namely, HKUST-1, MOF-5 and ZIF-8 (see Fig. 1.5).

HKUST-1 or Cu₃(BTC)₂ (BTC= 1,3,5-benzenetricarboxylic acid), which exhibits a facecentered cubic crystal structure that contains an intersecting three-dimensional (3D) system, was first reported by Chui et al. in 1999.^[21] The interaction of metal SBUs of tetragonal symmetry (paddle-wheel complexes) with C₃-symmetric BTC ligands results in a cubic network with three types of square-shaped pores (larger pore, 1.35 nm; middle pore, 1.1 nm; and small pore, 0.5 nm). HKUST-1 has a favorable degree of thermal stability (up to 230 °C) and an alternative face-centered cubic close packing of the large and middle cavities with a large Langmuir surface area

(917.6 m²g⁻¹).

MOF-5 or $Zn_4O(BDC)_3$ (BDC= 1,4-benzenedicarboxylate acid), which is another widely investigated MOF, was first reported by Yaghi et al. in 1999.^[14] MOF-5 shows a three-dimensional intersecting channel structure with 1.3 nm spacing between the centers of adjacent clusters. Its high thermal stability (up to 450 °C), high porosity (55.8%), and large Langmuir surface area (2630 m²g⁻¹) are promising properties that make MOF-5 suitable for a broad range of applications.

Zeolitic imidazolate framework (ZIF), especially ZIF-8, is another important MOF series material which was first reported by Yaghi et al. in 2006.^[44] ZIF-8 exhibits high permanent porosity (Langmuir surface area=1.810 m²g⁻¹), high thermal stability (up to 550 °C), and remarkable chemical resistance to boiling alkaline water and many organic solvents.



Figure 1.5 The structure of HKUST-1 (Figure taken from Ref.^[45]), MOF-5 (*Figure taken from Ref.*^[26]), ZIF-8 (*Figure taken from Ref.*^[46]).

1.1.4 Application of MOFs

MOF materials exhibit remarkable physical and chemical properties, such as significant thermal stability (over 200 °C), high porosity (over 50%), and high Langmuir surface area (from 1000 m^2g^{-1} to 10000 m^2g^{-1}). These characteristics facilitate their worldwide application in research laboratories and industries.

MOF materials have been comprehensively investigated. Numerous reports have focused on developing novel networks with different crystal sizes and shape topologies, as well as on their potential applications (e.g., hydrogen and methane storage,^[47, 48] CO₂ capture,^[49] removal of harmful and toxic chemicals,^[50] heterogeneous catalysis,^[51] luminescence,^[52] and metal corrosion inhibition^[53]). These potential applications of MOF materials have been mainly devoted to academic concerns. However, most applications remained at the stage of a research laboratory. Further experimental studies are required to obtain a deeper understanding of the properties of various MOFs for fundamental research and

technological perspectives.

Several applications of MOF-based materials have been achieved from academia to industry transposition in the last few years. BASF is the first company that successfully achieved the large-scale production of MOF-based materials in 2012 [Striking examples are MTA1 (AI-based MOF), MTA2 (ZIF-8), MTA3 (ZIF-67), and MTA4 (HKUST-1)].^[54]

1.2 MOF thin films: preparation and applications

MOF thin films have attracted an increasing amount of attention because their optical, electrical, tribological, wetting or biological properties can be adjusted to improve or change the properties of the MOF surface, contrary to the numerous powder metal organic frameworks prepared by solvothermal technique.^[55, 56] Many methods, such as growth/deposition from solvothermal mother solutions, ^[57, 58] liquid (LPE),^{[59,} 60] deposition,^[32] microwave-induced thermal phase epitaxy Langmuir-Blodgett,^[13] evaporation induced crystallization,^[61] colloidal deposition,^[62] electrochemical synthesis,^[63] reactive seeding^[64] and gel-layer synthesis,^[65] have been developed to prepare MOF thin films. In this section, major preparation methods of MOF thin films are introduced.

1.2.1 Preparation method of MOF thin films

1.2.1.1 Growth/deposition from solvothermal mother solutions

This straightforward approach, which is based on the conventional MOF synthesis scheme using solvothermal method, was used in the first successful preparation of well defined MOF thin films. The synthesis of MOF in this method is similar to the powder solvothermal method. The crystal size of MOF in the "mother solution" should be carefully adjusted to optimize the crystallization reaction using temperature, concentration of reactants, pH value, heating time, heating and cooling rates. A suitable functionalized surface should first be chosen to obtain MOF thin films.

Hermes et al. have employed a more sophisticated scheme to prepare MOF-5 thin film by immersing a COOH- terminated self-assembled monolayer (SAM) on Au wafer into nanometer-sized MOF-5 nuclei containing the "mother solution" (Fig. 1.6a).^[57] The optical micrographs in Fig. 1.6b illustrate the formation of MOF-5 cubes (with sizes 1-10 μ m) anchored rigidly on the functionalized surface. The X-ray diffraction (XRD) data shown in Fig. 1.6c demonstrate that the deposited material is MOF-5.



Figure 1.6 (a) The concept of anchoring a typical MOF-5 building unit to a carboxylic acid-terminated SAM. (b) Optical microscope (left) and an AFM image (right) of a selectively grown film of MOF-5 on a patterned SAM. (c) A PXRD pattern of Pd@MOF-5@SAM is shown in comparison to a sample of an authentic polycrystalline MOF-5 (trace below) (Figure taken from Ref.^[57]).

Bein et al. reported a more interesting experiment to achieve growth of highly oriented and crystalline MOF thin films on different types of functionalized substrates, in contrast to the preparation of the polycrystalline MOF thin films, as described above (Fig. 1.7a).^[58] The core strategy of this MOF thin film is the use of SAMs with different terminations to control the growth of HKUST-1 MOF on the corresponding crystallographic direction. For example, only the peaks belonging to the (001) crystallographic direction were observed in the case of COOH- terminated SAM. However, the situation was quite different for the case of the OH- terminated SAM, in which only (111) crystallographic direction was seen in this type HKUST-1 thin film (Fig. 1.7b).



Figure 1.7 (a) Schematic illustrations of oriented growth of HKUST-1 nanocrystals

controlled via surface functionalization on an 11-mercaptoundecanoic acid (up), and 11-mercaptoundecanol (down) gold surfaces. (b) X-ray diffraction patterns of thin films of $Cu_3(BTC)_2$ on functionalized gold surfaces, compared with a randomly oriented $Cu_3(BTC)_2$ powder sample measurement (Figure taken from Ref.^[58]).

1.2.1.2 Liquid phase epitaxy (LPE) of SURMOFs

Liquid phase epitaxy (LPE) is another major method used to easily prepare MOF thin films on functionalized substrates. Using this method we can directly grow highly ordered, crystalline MOF thin film on modified substrate via step-by-step approach at mild conditions, contrary to the growth/deposition from solvothermal mother solutions. The crystallographic direction of SURMOFs can be controlled by employing SAMs formed on substrates with different types of functional terminal groups.

Shekhah et al. prepared HKUST-1 thin films by sequentially immersing a COOH- or OH- terminated SAM modified Au substrate first into a Cu(OAc)₂ ethanol solution and then into a BTC ligand ethanol solution.^[59, 60] The substrate was rinsed after each step to remove unreacted components. Finally, the SURMOF was gradually fabricated through repetition of this process (Fig. 1.8a). The XRD data clearly demonstrated that the growth of HKUST-1 MOF proceeds along the (001) crystallographic direction using a COOH- functionalized Au substrate and on an OH- terminated surface MOF-layer with a (111) orientation (Fig. 1.8b).



Figure 1.8 (a) Schematic of the step-by-step approach for the growth of the SURMOFs on a SAM-functionalized substrate. (b) Out-of-plane XRD data for $[Cu_3(BTC)_2(H_2O)_3]$. a) Powder, b) growth on a MHDA SAM (calculated), c) growth on MHDA SAM

(experimental), d) growth on MUD SAM (calculated), e) grown on MUD SAM (experimental) (Figure taken from Ref.^[59]).

The growth of HKUST-1 on 16-mercaptohexadecanoic acid (MHDA) and 11-mercapto-1-undecanol (MUD) SAMs was further characterized via the step-by-step approach. The authors performed investigations using quartz crystal microbalance (QCM) with dissipation (Fig. 1.9), in which the increase in the mass of deposited molecular species on Au sensor surface can be monitored. The data showed a stepwise increase in the mass of the deposited layers with subsequent addition of Cu(OAc)₂ and the ligand H₃BTC.



Figure 1.9 QCM-D signal as a function of time recorded in situ during sequential injections of Cu(Ac)2, ethanol and H3btc on the QCM substrate covered by a MHDA SAM (left), and a MUD SAM (right) (Figure taken from Ref.^[60]).

1.2.1.3 Microwave-induced thermal deposition

Jeong et al. demonstrated a rather straightforward approach for the selective patterned deposition of MOF-5 crystals on substrate.^[32] The substrates coated with a conductive thin-film layer were vertically placed in vials containing the MOF-5 precursor mother solution. MOF-5 crystals were subsequently grown under microwave irradiation in a domestic microwave oven with 500 W power for 5-30 s.

The patterns of MOF-5 crystals prepared on carbon-patterned AAO substrates within 30 s, demonstrating the ability of this microwave-induced thermal deposition method to rapidly generate patterns (Fig. 1.10a). The XRD data shown in Fig. 1.10b demonstrate that the deposited material is MOF-5.



Figure 1.10 (a) SEM images of a) patterned growth of MOF-5 crystals on patterned C-AAO substrates using a TEM grid and b) a multi-layer MOF/silicalite-1 on Au-AAO. Inset image in figure b) is from the underlying silicalite-1 layer. (b) XRD pattern of MOF-5 thin film grown on G-AAO as compared with that of MOF-5 powder prepared under MW and a calculated pattern based on single crystal MOF-5 structure (Figure taken from Ref.^[32]).

1.2.1.4 Langmuir-Blodgett method

Langmuir-Blodgett technique is an excellent method for fabricating organic films by depositing well-ordered monolayer of an organic material from the surface of a liquid onto a solid substrate. This technique has been applied to various functional molecular systems, resulting in the successful assembly of well-organized 2D arrays.^[66]

Makiura et al. prepared a highly-oriented, defect-free copper-mediated CoTCPP 2D array thin film onto unmodified silica and quartz substrates using Langmuir-Blodgett method (Fig. 1.11).^[13] The copper-mediated CoTCPP 2D array monolayer adsorbs homogeneously with each immersion step, forming films with highly accurate thickness. The total thickness of a Langmuir-Blodgett film can be accurately determined because the thickness of each monolayer is known.



Figure 1.11 Schematic illustration of the fabrication method of NAFS-1. The repetitive process of successive sheet deposition and rinsing/solvent immersion leads to the sequential layer-by-layer growth of NAFS-1 with any desired thickness (Figure taken from Ref.^[13]).

1.2.1.5 Evaporation induced crystallization

Evaporation-induced crystallization is a particularly simple method for producing MOF crystallite thin films on different substrates. This method is based on MOF nuclei containing the "mother solution," similar to the first method discussed in section 1.2.1.1 above.

Vos et al. employed soft lithographic techniques to deposit monodispersed HKUST-1 crystals in patterns down to the single-crystallite level by in situ crystallization (Fig. 1.12).^[61] Moreover, the deposited crystals were highly oriented and displayed physical boundaries formed during crystallization.



Figure 1.12 (a) Schematic of nucleation, growth, and orientation of HKUST-1 crystals in confinement during solvent evaporation. (b) Characterization of HKUST-1 prepared from precursor solution by evaporation. A) Powder XRD pattern. B) SEM image. D) Thermogravimetric analysis, showing exclusively water desorption (37 wt%) at a temperature of T<600 K (Figure taken from Ref.^[61]).

1.2.2 Application of MOF thin films

1.2.2.1 QCM-based sensors

The most simple and direct application of MOF thin films is for the monitoring of the change in mass of loaded guest molecules using QCM. This approach is based on coating a QCM sensor substrate with MOF thin films of varying thicknesses. Numerous studies have already demonstrated during the past decade the application of MOF thin films on sensors for detecting changes in the concentration of guest molecules by loading or depletion, in particular for the sensor used in QCM devices. QCM-based MOF thin-film sensors have considerable advantages over powder MOFs because they can be easily prepared and are relatively stable. QCM-based MOF thin-film sensors can generally be classified into three main types according to their different applications, namely, for gas storage, gas separation, and measurement of

diffusion coefficient in MOFs.

Heinke et al. recently reported a SURMOF-based hybrid system with photoswitchable azobenzene side groups for gas adsorption and storage.^[67] A two-layer MOF on an MOF system with a passive bottom layer $Cu_2(bpdc)_2(bipy)$ and a photo-switchable top layer $Cu_2(azo-bpdc)_2(bipy)$ (azo-bpdc: 3-azobenzene-4,40biphenyldicarboxylate) has been synthesized on the QCM sensor surface by LPE. Gas molecule storage and releases on SURMOF are realized by illumination with visible light (Fig. 1.13). Specifically, the bottom layer acts as a molecular container, and the top layer serves as a valve. The switching of the azobenzene groups from its basic *trans* state (open state, by UV light) to the *cis* state (close state, by red light) could control the adsorption and storage of gas molecules within MOF thin films.



Figure 1.13 (a) Optically triggered release from two-component SURMOFs. (b) Sketch of the layered photoswitchable SURMOF. (c) Release of the prototypemolecule (butanediol, BD) from a two-layered, photoswitchable SURMOF determined by a quartz crystal microbalance. Beginning at the time indicated by the red arrow, the sample is irradiated with light at 560 nm wavelengths (Figure taken from Ref.^[67]).

Tu et al. reported a similar experiment in which reactive NH₂ functional groups were incorporated at the top layer of the MOF thin film, and the performance for selective adsorption was studied.^[68] An MOF on an MOF system with a passive bottom layer $Cu_2(bdc)_2(dabco)$ and an active top layer $Cu_2(NH_2-bdc)_2(dabco)$ is shown in Fig. 1.14. The NH₂ groups in the top layer allow subsequent modification with tert-butyl isothiocyanate (*tert*-BITC). The adjusted pore structure within the material by the combined *tert*-BITC presents remarkable effects on the transmittance of cyclohexane molecules, but no negative effects on hexane molecules.



Figure 1.14 Schematic illustration of programmed functionalization of SURMOFs via liquid phase heteroepitaxial growth and post-synthetic modification: initially, SURMOF [Cu₂(bdc)₂(dabco)] (A) was deposited on pyridyl-terminated SAM on Au covered QCM substrates using the LPE method. Sequentially, SURMOF [Cu₂(NH₂-bdc)₂dabco] (B) was deposited on A using the LPE procedure giving rise to SURMOF B@A. Finally, SURMOF B@A was modified by post-synthetic modification with tert-butyl isothiocyanate (tBITC) (Figure taken from Ref.^[68]).

In 2010, Zybaylo et al. reported the first study that used QCM-based sensor to determine the diffusion constant in MOFs.^[69] The authors used an HKUST-1 thin film grown on gold QCM sensor surfaces by LPE. The homogeneous, highly ordered, and thickness-controlled SURMOFs were appropriate for analyzing the QCM data using Fickian diffusion to yield the diffusion constant. The authors calculated the diffusion coefficient of the pyridine diffusion into HKUST-1 at room temperature, and the coefficient was $1.5 \times 10^{-19} \text{ m}^2 \cdot \text{s}^{-1}$. This fairly simple and straightforward method can help measure the diffusion coefficients of molecules within MOFs.



Figure 1.15 Data trace of a QCM experiment on HKUST-1 (20 deposition cycles). (a): normalized shifts of frequency ($\Delta f/n$) and bandwidth ($\Delta \Gamma/n$) vs. time. Pyridine is removed from the gas stream and t = 84 min. (b) Mass loading (averaged over the three harmonics shown in (a)) vs. square root of adsorption time. The dashed line is a fit to Fickian diffusion. From the slope at small times, one estimates the diffusion coefficient as D ~ 1.5 × 10⁻¹⁹ m² s⁻¹ (Figure taken from Ref.^[69]).

1.2.2.2 Drug delivery

Drug delivery is another interesting area for MOF thin films. Low stability of acids and bases usually restricts the application of MOF thin films in biological science and pharmacy.

Tsotsalas et al. reported a new type of material, namely, SURGEL, which was obtained by covalent cross-linking of MOF ligands via click chemistry (Fig. 1.14).^[70] This process yielded robust SURGEL thin films which corresponded to SURMOFs and showed high stability under biological conditions. These thin films have been successfully used in drug delivery. SURGELs are considered as substrates that can be used to deliver biomolecules to the interior of adhering cells. The fabricated SURGEL was first loaded with arabinose and subsequently exposed to bacterial cells that were gene-modified with an arabinose-triggered GFP switch. Induction of GFP expression has proved to be highly site-specific; expression occurred only for those bacteria in direct contact with the SURGEL substrate.



Figure 1.14 (a) Schematic representation of the cross-linking process within the SURMOF-2 structure. (b) Schematic representation and fluorescence microscopy images after 24 h of incubation in the presence of SURGEL substrates (Figure taken from Ref.^[70]).

1.2.2.3 Selective sensor for chemical vapors and gases

The third low-cost and rather straight-forward application is the use of thin films with different thicknesses to monitor the loading of these porous coatings with guest molecules.

Lu et al. reported that ZIF-8 MOF thin films with different thicknesses show different colors because of the constructive and destructive interference of light beams reflected from the upper surface of the substrate (Fig 1.15a).^[71] In addition, loading of ZIF-8 MOF thin films by guest molecules can change the optical constant of the MOF material itself, and the surface color subsequently changes. The change in the color of ZIF-8 MOF thin films was analyzed by loading guest molecules. The authors presented constructed MOF-based Fabry-Perot devices that act as selective sensors for chemical vapors and gases. Incorporating any polarizable molecules into the cavity of MOF will displace vacuum and increase the overall refractive index. This process results in red shifts of the interference peaks (Fig 1.15b).



Figure 1.15 (a) Photograph of a series of ZIF-8 films of various thicknesses grown on silicon substrates. (b) (A) UV-vis transmission spectra of 10-cycle ZIF-8 film grown on glass substrate after exposure to propane of various concentrations (blue curve for 0% and red curve for 100%) and (B) corresponding interference peak (originally at 612 nm) shift versus propane concentration. The propane concentration is expressed as a percentage of the total gas flow where nitrogen is used as diluents (Figure taken from Ref.^[71]).

1.3 Surface-mounted metal-organic frameworks (SURMOFs)

This thesis was aimed to prepare and apply SURMOFs using LPE growth on functionalized substrates (see Fig. 1.16). The detailed process was discussed in section 1.2.1.2. The LPE method can suitably control the thickness (normally nanometer range) of the MOF thin film via layer-by-layer growth method. The other important feature of this technique is the growth of homogeneous, highly oriented, and highly crystalline SURMOFs.



Figure 1.16 schematic of the step-by-step growth MOFs on substrate.

1.3.1 Substrate

In principle, MOFs can be grown on any smooth and functionalized substrate surfaces. However, only a limited number of solid materials, such as gold, silver, silicon, alumina, glass, quartz glass, FTO, and metallic oxide (Fig. 1.17), have been successfully used to prepare SURMOFs. A range of surface treatments are required for all substrates to meet the conditions of growing different MOFs on the substrate surface. However, inhomogeneous, mixed-oriented, and polycrystalline MOFs will be obtained on the substrate with pronounced surface defects and relatively high roughness.



Figure 1.17 Pictures of different types substrates.

Functionalization of a substrate through a chemical or physical process depends on the substrates used and the required functional groups. For example, gold wafer post-grafted with specific functional group molecules may form SAM through chemisorptions of thiol-terminated molecules, such as MHDA (COOH-)^[72], (4-(4-pyridyl)phenyl)-methanethiol (PP1, pyridyl)^[73] or MUD (OH-). Further details are discussed in section 3.1.2.

1.3.2 Methods

Several techniques, such as spray,^[74] pump,^[75] dipping^[76] and QCM^[77] method have been established to prepare SURMOFs. They will be described in the following.

1.3.2.1 Spray method

A straightforward approach based on the layer-by-layer MOF synthesis scheme was employed in the rapid and successful preparation of well-defined SURMOF thin films on a functionalized substrate. The four-step method was performed as follows: (1) the metal solution was sprayed on the substrate; (2) the substrate was rinsed with pure ethanol to remove residual reactants; (3) ligand solution was sprayed on the substrate; and (4) the substrate was further rinsed with pure ethanol. The number of spray cycles was dependent on the experimental requirements (Fig. 1.18).

The spray method (LEP process) has become one of the widely used methods to prepare SURMOFs because of its short time consumption, high automatic intensity, mild reaction condition, and remarkable saving solution. Several important SURMOFs, such as Cu₃(BTC)₂, Cu(BDC), and Cu(BPDC), have been successfully prepared by the spray method through four years of development. However, other complex three-dimensional SURMOFs, such as Cu₂(BDC)₂(dabco) and Cu₂(BPDC)₂(dabco), have not been successfully prepared. This method should be further improved in the future to avoid pitfalls. Controlling temperature and humidity using a vacuum glove-box system should be considered.



Figure 1.18 schematic of the setup employed for the fabrication of MOF thin films with the spray method: (1) Gas supply, (2) gas flow controller (3) three-way valve gas distributor (4) (A, B, C) solutions storage containers (5) sample holder (6) dosing valves, (7) spray chamber, (8) PC (Figure taken from Ref.^[74]).

1.3.2.2 Pump method

Pump method is another major technique that facilitates the preparation of SURMOF thin films. This system is controlled by a central computer, and a thermostatic oil bath is employed to precisely control the temperature. Compared with the LPE spray method, similar four steps are employed in this method: pumping of metal solution, rinsing with pure solvent, pumping ligand solution, and rinsing with pure solvent again (Fig. 1.19). These steps are repeated up to the required number of times.

The pump method can control the temperature of a system in a wide range, in contrast to the spray method. In addition, MOF growth on the surface can be

improved by increasing reaction time after each step. More interestingly, we successfully prepared several three-dimensional SURMOF with complex structures, such as $Cu_2(BDC)_2(dabco)$ and $Cu_2(BPDC)_2(dabco)$, which cannot be prepared by the spray method. However, this method is limited by its long preparation time and low yield. Additionally, some known MOFs, such as Cu(BDC) and Cu(BPDC), cannot be fabricated using this method.



Figure 1.19 Schematic diagrams for the automated LBL growth of MOFs thin films on substrates functionalized with SAMs. The preparation is done by repeated immersion cycles first in solution of the metal precursor and subsequently in the organic ligand solution, with solvent rinsing in between (Figure taken from Ref.^[75]).

1.3.2.3 Dipping method

The dipping method was the first successful LPE method that has been used to prepare SURMOF thin films. The core parts in the dipping system are four containers with three different solutions (metal, ligand, and two rinsing solutions). A robot control system has recently been developed (Fig. 1.20). The following steps were conducted in the dipping method: (1) substrate was placed in the metal solution for a few minutes; (2) substrate was removed and immersed in rinsing solution; (3) substrate was immersed in ligand solution for few minutes; and (4) substrate was immersed in another rinsing solution. Thus, SURMOF thin films with different thicknesses were prepared by repeating the steps of the dipping method.

Dipping method has advantages, such as simple preparation, adjustable operating time, and low consumption of solvent, similar to the pump method. The main

difference between the dipping method and the pump method is that the former can be cleaned using an ultra-sonic cleaner after each step but the temperature cannot be controlled. Therefore, samples prepared by using the dipping method are more homogeneous than those prepared by other methods.



Figure 1.20 The setup of the dipping robot. PO: starting and final position for the sample holder; P1eP7: containers for immersion solutions; 1: Teflon working table; 2: container lid; 3: gripper; 4: sample holder; 5: sample; 6: position controller; 7: ultrasonic bath; 8: shower; 9: parking position of container lid; 10: pump and solution bottle for showering; 11: computer (Figure taken from Ref.^[76]).

1.3.2.4 Quartz crystal microbalance (QCM) method

QCM measures a mass variation per unit area by monitoring the change in frequency of a quartz crystal resonator. It can be used to monitor the mass increase of deposited molecular species on Au sensor surfaces. Gradual addition of metal and ligand solutions lead to stepwise increase of the deposited layers in mass, which corresponds to the layer-by-layer growth of SURMOF on the sensor surface (Fig. 1.21).

A major advantage of QCM is the possibility to continuously monitor the SURMOF growth process. Another interesting point is that the synthesis can be conducted at different temperatures (20 °C–60 °C). In addition, this method can be directly used for other experiments, such as monitoring of adsorption/desorption of gas or liquid molecules into SURMOFs. However, the application of QCM sensor is limited by high cost, long preparation time, and low yield.



Figure 1.21 Schematic of quartz crystal microbalance (QCM) method for SURMOF preparation.

1.3.2.5 Conclusion

In summary, we introduced four main methods to grow SURMOFs on the functionalized substrates. All above four methods are based on LPE technology. Therefore, using these methods the size and thickness of SURMOFs can be controlled. In addition, these methods exhibit others common advantages including short time consumption, high automatic intensity, mild reaction condition and oriented crystalline. In Table 1.1, we summarize the strength and weakness of each method in terms of temperature, time, preparation efficiency, yield, product variety and so on.

Table 1.1 In contrast of spray method, pump method, dipping method and QCM method.

	Spray method	Pump method	Dipping method	QCM method
Temperature	RT	All	All	20-60 °C
Time ¹	40-60 min	15 h	15h	20h
Type of MOF ²	Most of 2D MOF	Most of3D MOF	Most of 3D MOF	Most of 3D MOF
Substrate	All	All	All	QCM sensor
Ultra-sonic cleaner	No	No	Yes	No
Consumption of solvent ³	~200 ml	~100 ml	50 ml	~100 ml

^{1,3} Take the case of prepared 30 layers HKUST-1 SURMOF as a example;

² Here is means the method is more suitable to prepared 2D or 3D MOF.

1.4 Metal ions and NPs embedded into MOFs

MOF materials with relatively high thermal stability and flexible pore sizes have provided an ideal platform to encapsulate catalytically active compounds (such as Pt,^[78] Au,^[79] and Ti^[80]). Various metal@MOFs with different content, position, shape and distribution of guest molecules inside MOF could be obtained by controlling and selecting the different loading methods. The following section will briefly describe a number of different methods employed for the preparation of metal ions and NPs inside MOFs.

1.4.1 Metal ions embedded into MOFs

Many methods, such as solution impregnations,^[81] chemical vapour deposition (CVD),^[82] incipient wetness impregnation,^[83] solid grinding^[79] and atomic layer deposition (ALD)^[84] have been developed to prepare metal-ions@MOFs in the last two decades. In general, the synthesis methods of metal-ions@MOFs can be divided into two categories according to the distribution of guest metal ions inside MOF: random distribution and self-assembled deposition.

In the first category, the metal ions diffuse into the framework of MOFs and adsorb at the phenyl ligands of MOFs (usually benzene ring). As a result, the distribution of metal ions inside MOF shows a random character due to the weak interaction between guest molecules and MOFs.

Heinke et al. reported a quantitative study of the adsorption and diffusion of ferrocene (FC) into $Cu_2(ndc)_2(dabco)$ MOF thin film by using a QCM at different temperatures.^[85] The uptake curves in the QCM-data show that FC molecules were successfully loaded into SURMOFs with a concentration of 0.19 FC per pore at 305 K and 0.06 FC per pore at 335 K, respectively. In addition, based on the uptake rates they determined the diffusivity $(10^{-19} \text{ to } 10^{-17} \text{ m}^2 \cdot \text{s}^{-1})$ and activation energy(90 kJ·mol⁻¹) of the FC loading process .



Figure 1.22 Schematic of the loading ferrocene into Cu₂(ndc)₂(dabco) SURMOF (lift)

and uptake curves measured by QCM in the temperature of 305 K (right) (Figure taken from Ref.^[85])

Another category regarding the synthesis of metal-ions@MOFs is directional adsorption of self-assembled guest metal ions with nucleation centers in MOFs.

Hupp et al. reported a technique to form a highly stable cobalt sulfide functionalized MOF, CoS-AIM, by using the ALD deposition of cobalt sulfide into NU-1000.^[84] In this work, the Co(amd)₂ [bis(N,N'-di-*i*-propylaceta- midinato)-cobalt(II)] and H₂S were used as precursor to form CoS_x inside NU-1000 MOF. Spectroscopic techniques confirm an uniform and self-assembled deposition of cobalt sulfide throughout the crystallites, without loss in crystallinity or porosity. This material was found to display excellent catalytic activity for the selective hydrogenation of nitroaromatic compounds to amines.



Figure 1.23 Representative structure of NU-1000. Circles highlight the Zr_6 node and the pyrene linker. ALD of 1 AB cycle of cobalt sulfide produces cobalt sulfide functionalized NU-1000 with approximately one CoS_x site per Zr_6 node (Figure taken from Ref.^[84]).

1.4.2 Metal NPs embedded into MOFs

Loading of MOFs with metal NPs is a more promising field of research in catalysis compared to the metal-ions@MOFs. One useful strategy for embedding metal NPs inside MOFs is using metal precursor solutions. MOFs are excellent templates to provide confined space that limits the particle growth and impedes the agglomeration of formed NPs. The preparation process of metal NPs includes initial diffusion of metal precursors into MOFs. The metal NPs can be produced via decomposition or reduction of the metal precursors. Thus, the dimension and shape of the NPs, synthesized directly in the pores of the framework, should be controlled

by the pore size, shape, and channel structure of the host materials (Fig. 1.24).



Figure 1.24 General strategy employed for loading of MNPs inside MOFs (Figure taken from Ref.^[86])

Xu et al. reported a technique to deposit of Au NPs into a zeolite-type MOF by a simple solid grinding method.^[79] In this work, the $(CH_3)_2Au(acac)$ (acac= acetylacetonate) was used as precursor to form Au NPs via H₂ reduction. ZIF-8 was employed as an ideal platform to encapsulate catalytically active Au NPs. This AuNPs@ZIF-8 material exhibited considerable catalytic activityfor CO oxidation to CO_2



Figure 1.25 Conversion-temperature curves for CO oxidation over Au@ZIF-8 catalysts with different Au loadings (left) after repeated catalytic runs. TEM images of 1.0 wt % (a and b) and 5.0 wt % (c and d) Au@ZIF-8 before (a and c) and after (b and d) catalytic reaction (right) (Figure taken from Ref.^[79]).

Another methodology is directly loading preformed metal NPs into SURMOFs. The NPs were stabilized by using organic molecules, surfactants and polymers as capping agents.

Wöll et al. reported the fabrication of hybrid yet well-ordered porous NP arrays with

full 3D periodicity by embedding nanometersized metal–organic clusters (MOCs) into MOFs.^[87] A maximum loading efficiency of one NP per pore was achieved by using LPE approach. The loading of an achiral HKUST-1 SURMOF with preformed NPs, homochiral $Ti_4(OH)_4(R/S-BINOL)_6$ clusters (Ti-MOC, BINOL = 1,1'-bi-2-naphthol), leads to the formation of a regular lattice inside the pores of SURMOFs. Exposure to the different enantiomers of methyl lactate revealed that the NP@MOF metacrystal is quite efficient regarding enantiomer recognition and separation.



Figure 1.26 (a) Powder MOC loaded MOF prepared by mixing reagent of Cu(OAC)₂, H₃BTC, and MOC using solovothermal method (unsuccessful) (b) Powder MOC loaded MOF prepared by immersing powder MOF into MOC solution (unsuccessful). (c) Generic encapsulation of guest into MOF thin film via direct immersing approach (unsuccessful). (d) Layer-by-layer encapsulation of guest into MOF thin film via in situ LPE approach (successful). (e) Schematic presentation of in situ layer-by-layer growth of enantiopure Ti-MOC-loaded HKUST-1 thin film using the liquid phase epitaxy (LPE) approaches (Figure taken from Ref.^[87]).

1.5 Loading metal ions and NPs into SURMOFs

SURMOFs not only exhibit the advantages of the powder MOFs, but also show significant performance of highly ordered, size and thickness controlled as well as directional growth on substrates.^[58, 59] Loading of metal ions or NPs inside SURMOFs is promising for catalysis, optical, electrical and electrochemical applications. The major aim of this thesis is to discuss the methodology of loading metal ions and NPs into SURMOFs, using the following three main approaches.

The first methodology of embedding metal-precursors inside an MOF network is based on the use of ligands as nucleation centers (see sections 4.1 and 4.2). Phenyl
compounds are the most commonly used ligands. Benzene ring has three delocalized π orbitals spanning all six carbon atoms, thereby contributing to the improvement of metal ion adsorption.^[88] The interaction between the benzene ring and guest molecules is relatively weak. Additionally, the flexible pore sizes and interlinking open pore structures of the MOFs also help increase the embedding of guest metal ions.

A second approach to the synthesis of modified MOFs is using a functionalized ligand to increase the number of nucleation centers (see section 5). The functionalized ligand does not change the crystal structure of the host materials, but improves their adsorption ability of metal ions. For example, sulfur-MOF-5 can be obtained by the addition of sulfur-conjugated functional groups on the BDC linker, thereby improving the metal uptake process because the sulfur unit has strong adsorption ability for metal ions.^[25]

The third important approach is using open coordination sites (OCSs) at the metal center to modify the adsorption of metal ions (see section 6). MOFs with OCSs at the metal center exhibit effective adsorption of small organic molecules, such as H_2O , NH_{3} , and CH_2Cl_2 .^[89-91] A metal complex with small organic molecules can be attached to the OCSs to utilize these OCSs. Thus, metal ions are directed to loading onto the pores of MOFs.

2 Characterization methods

Surface analysis techniques play a crucial role to achieve the main objective of this thesis. Several key surface analytical techniques were used in this thesis: X-ray diffraction (XRD), infrared (IR) spectroscopy, Raman spectroscopy, ultraviolet–visible (UV-vis) spectroscopy, X-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), transmission electron microscopy (TEM), quartz crystal microbalance (QCM), and electrochemistry at semiconductor electrodes.

2.1 X-ray diffraction

The XRD crystallography of a crystalline material was first discovered by Laue in 1912. This method is well established and is widely used to characterize materials. XRD is commonly used to obtain information on the atomic distribution of crystalline materials, such as salts, metals, minerals, semiconductors, and various inorganic, organic, and biological molecules.^[92] In addition, this technique can be used to investigate thin crystalline films by identifying the relative angles and intensity of diffracted X-ray peaks. Furthermore, we can estimate the possible location of guest molecules in a known crystal based on changes in the XRD peaks before and after loading.

2.1.1 Theoretical background

XRD can be used to identify the atomic and molecular structure of an unknown crystal. Atoms in crystals will cause X-ray scattering in specific directions upon illumination by a beam of incident X-rays. If incident X-rays at a certain wavelength (λ) strike at a stated angle (θ) onto a crystal where all atoms are placed in a regular periodic array with inter-planar spacing (*d*) (Fig. 2.1), the XRD detector will record diffracted peaks according to Bragg's law, as follows:

$$2d\sin\theta = \lambda \tag{1}$$

Diffraction patterns of the sample can be obtained because of the random orientation distribution of crystals in powder samples. Moreover, the positions of the atoms in the crystal can be determined by measuring the intensities of the diffracted peaks as function of 2θ angles (0°–90°).



Figure 2.1 Schematic of X-ray diffraction by a crystal (Bragg condition).

The basic design of the XRD apparatus, illustrated in Fig. 2.2, highlights three main components, namely, the X-ray source (F), sample holder (S), and detector (G), positioned on the circumference of a circle. A sample in the flat-plate form is usually positioned on the ω -axis corresponding to the center of the diffractometer. During measurement, the 2 θ -axis rotates twice as much as the ω -axis, hence commonly referred to as a "theta two-theta scan".



Figure 2.2 Para-focusing geometry and some essential points of an X-ray diffractometer. (Figure taken from Ref.^[92]*)*

2.1.2 Estimation of X-ray diffraction intensity

A crystal is defined as a solid consisting of atoms arranged in a periodic pattern defined by the unit cell. The XRD peak intensity is directly related to the position of the atom in the unit cell. Therefore, the information of the phase differences based on the relationship between the scattering intensity and the atomic positions in one unit cell should be determined when the scattering intensity from crystals is considered. The sum of the scattered waves from the atoms in a unit cell (structure factor F) can be computed using the following generalized equation:^[92]

$$\left|F_{(hkl)}\right|^{2} = F_{hkl}F_{hkl}^{*}$$
$$= \left[\sum_{j=1}^{N} f_{j}\cos 2\pi (hx_{j} + ky_{j} + lz_{j})\right]^{2} + \left[\sum_{j=1}^{N} f_{j}\sin 2\pi (hx_{j} + ky_{j} + lz_{j})\right]^{2}$$
(2)

where *hkl* represents the crystallographic planes, *N* represents the total number of atoms in a unit cell, f_j represents the atomic scattering factor of the *j*-th atom in the corresponding unit cell, and (*x*, *y*, *z*) represents the atomic coordinates.

The structural factor *F* is generally given by a complex number. This factor represents the amplitude and phase of the scattered wave obtained from the summation of all atoms in the unit cell. The usefulness and application of Equation (2) can be fully appreciated by evaluating some actual cases. For example, the structure factors of (001) and (002) for the body-centered cell HKUST-1 are given as follows:

$$\left|F_{HKUST-1(001)}\right|^{2} = \left[\sum_{j=1}^{48} f_{Cu_{j}} \cos 2\pi z_{j}\right]^{2} + \left[\sum_{j=1}^{48} f_{Cu_{j}} \sin 2\pi z_{j}\right]^{2} = 0$$
$$\left|F_{HKUST-1(002)}\right|^{2} = \left[\sum_{j=1}^{48} f_{Cu_{j}} \cos 2\pi 2z_{j}\right]^{2} + \left[\sum_{j=1}^{48} f_{j} \sin 2\pi 2z_{j}\right]^{2} = \left[-12.90f_{Cu(002)}\right]^{2}$$

where f_{Cuj} represents the atomic scattering factor of the *j*-th Cu atom in the corresponding unit cell, and *z* represents the atomic coordinates in the *z*-axis. The position of Cu atoms in HKUST-1 unit cell is summarized in table 2.1.

The position of Cu atoms in HKUST-1 unit cell (48 atoms) (x, y, z)					
0,0.21,0.21	0,0.21,0.79	0, 0.29, 0.29	0, 0.29, 0.71	0, 0.71, 0.29	0, 0.71, 0.71
0,0.79,0.21	0, 0.79, 0.79	0.21, 0, 0.21	0.21, 0, 0.79	0.21, 0.21, 0	0.21, 0.29, 0.5
0.21, 0.5, 0.29	0.21, 0.5, 0.71	0.21, 0.71, 0.5	0.21, 0.79, 0	0.29, 0, 0.29	0.29, 0, 0.71
0.29, 0.21, 0.5	0.29, 0.29, 0	0.29, 0.5, 0.21	0.29, 0.5, 0.79	0.29, 0.71, 0	0.29, 0.79, 0.5
0.5, 0.21, 0.29	0.5, 0.21, 0.71	0.5, 0.29, 0.21	0.5, 0.29, 0.79	0.5, 0.71, 0.21	0.5, 0.71, 0.79
0.5, 0.79, 0.29	0.5, 0.79, 0.71	0.71, 0, 0.29	0.71, 0, 0.71	0.71, 0.21, 0.5	0.71, 0.29, 0
0.71, 0.5, 0.21	0.71, 0.5, 0.79	0.71, 0.71, 0	0.71, 0.79, 0.5	0.79, 0, 0.21	0.79, 0, 0.79
0.79, 0.21, 0	0.79, 0.29, 0.5	0.79, 0.5, 0.29	0.79, 0.5, 0.71	0.79, 0.71, 0.5	0.79, 0.79, 0

Table 2.1 The position of Cu atoms in HKUST-1 unit cell.

The results show that the reflections will be observed for planes of (002), but not the reflection for the planes (001) because its structure factor is equal to zero.

The structure factor *F* is an important parameter to understand the relationship between the crystal structure and the intensity of the diffracted X-rays from each crystallographic plane measured. In addition to the structure factor, the measured intensity of diffracted X-rays from powder samples is related to other various factors, such as polarization, multiplicity, Lorentz, absorption, and temperature factor.

The intensity of diffracted X-rays for powder crystalline samples can be described using a general formula considering the above-mentioned factors. For example, intensity *I* measured by a diffractometer with characteristic monochromatic radiation is given by the following equation:^[92]



2.1.3 X-ray diffraction of the MOF thin film

Contrary to a powdered sample, a thin film is generally formed two-dimensionally on the substrate surface and has large anisotropy either along the out-of-plane direction (thickness) or in the in-plane direction (within surface plane). We should characterize a thin film both along the out-of-plane and in-plane directions to ascertain the crystallinity and orientation of a thin film material (Fig. 2.3).



Figure 2.3 Schematic of the X-ray diffraction measurement of (a) out-of-plane and (b) in-plane of a thin film.

In this thesis, out-of-plane measurements of all samples were performed using a Bruker D8 Advance equipped with a Si-strip detector (PSD Lynxeye©; position sensitive detector) and Cu K $\alpha_{1,2}$ radiation ($\lambda = 0.15418$ nm) in ϑ - ϑ geometry, variable slit on primary circle. Scans were run over various 2ϑ ranges, with a step width of 0.024° and step time of 2 s, up to 5 s for higher order peaks. The 2ϑ angle scanning range was selected to be from 3° to 60° to observe the corresponding peaks of the deposited film.

The in situ, heated, out-of-plane XRD measurements were conducted using a PAAR HTK 1200 heating stage directly installed into the Bruker D8 Advance diffractometer. The heating rate was set to 1 °C/min, and the temperature range was set between 24 and 230 °C.

In-plane XRD was conducted using a Bruker D8 Discover equipped with a quarter Eulerian cradle, tilt-stage, and 2.3° Soller-slits installed on both sides. A Göbel-mirror and a PSD Lynxeye[©] in θ -2 θ geometry were applied.

The thin-film samples were measured directly, whereas the powdered samples were first pressed into tablet forms (from 0.1 μ m to 2 μ m thick).

2.2 Infrared spectroscopy

IR spectroscopy was the first structural spectroscopic technology widely used to identify and study chemicals since the conceptual breakthrough of an IR correlation chart in the 1950s and 1960s. This technique is readily available through commercial instrumentation. The IR technique utilizes an IR spectrometer (or spectrophotometer) to produce an IR spectrum characterizing the chemical bonding of a given sample, which can be solid, liquid, or gaseous. Common laboratory instruments used in this technique include transmission IR spectroscopy, IR reflection absorption spectroscopy (IRRAS), and attenuated total reflection (ATR).

2.2.1 Theoretical background

Two main factors, namely, radiation frequency and molecular dipole moment, influence the IR absorption process. The molecular vibration for molecular absorption of the incident IR photon energy must induce a change in the dynamic dipole moment. Fig. 2.4 shows the oscillating electric field of the IR radiation generating forces on the molecular dipole. The oscillating electric field drives the oscillation of the molecular dipole moment, alternately increasing and decreasing the dipole spacing.



Figure 2.4 The oscillating electric field of the photon generates oscillating, oppositely directed forces on the positive and negative charges of the molecular dipole. The dipole spacing oscillates with the same frequency as the incident photon. (Figure taken from Ref.^[93])

The dynamic dipole moments of uncharged molecules are derived from the partial charges of the atoms, which can be determined from molecular orbital calculations. Symmetric molecules or bonds have no dipole moments and therefore do not absorb IR radiation. For example, homonuclear diatomic molecules, such as H₂, N₂, and O₂, have no dipole moments and are IR inactive. By contrast, heteronuclear diatomic molecules, such as HCl, NO, and CO, have dipole moments. Thus, their corresponding vibrations are IR active.

More complex molecules contain more chemical bonds and correspondingly show more complex vibrational spectra. For example, CO_2 is a linear molecule with four vibrational modes (Fig. 2.5). However, the CO_2 symmetrical stretching is IR inactive because it has no dipole moment. The absorption spectrum of the samples can be recorded by measuring the IR absorption in the range of 400–4000 cm⁻¹, and the nature of the chemical bonds can be determined.



Figure 2.5 Four vibrational modes in the linear molecule CO_2 .

2.2.2 Transmission infrared spectroscopy

Transmission IR spectroscopy is one of the most common approaches for the chemical analysis of materials. Nearly any type of samples (e.g., solid, liquid, or gas) can be measured by transmission IR spectroscopy, with varying sample preparations. A major disadvantage of this method is the difficulty in sampling for some special samples. For example, powder samples should be mixed and formed into tablet with another powder that is IR transparent, whereas thin films and membranes can be directly analyzed using a sample holder.

2.2.3 Infrared reflection-absorption spectroscopy

IRRAS is an established analytical technique to characterize thin films or monolayers on substrate surfaces. The sample in IRRAS measurements is investigated in reflection geometry under grazing incidence (typically 80°). The sensitivity of this method can be significantly enhanced by employing the polarization modulation (PM) technique. In particular, atmospheric absorption of the samples caused by water vapor and CO₂ can be eliminated. The PM-IRRAS technique considers the different absorptions of p- and s-polarized light at large angles of incidence. The p-polarized plane is parallel to the plane of incidence, whereas the s-polarized plane is perpendicular to the plane of incidence (Fig. 2.6).



Figure 2.6 Principle of infrared reflection-absorption spectroscopy.

The ultrathin layers on metal surfaces (e.g., Au wafer) interact with the p-polarized fraction of light but not with the s-polarized one (Fig. 2.7a). However, for the ultrathin layers on the nonmetal surfaces, such as silicon or glass, the p- and s-polarized light will both affect IR reflection (Figs. 2.7b and c).



Figure 2.7 Calculated reflectivity differences between the clean substrate (R_0) and adsorbate- covered substrate (R_F) for different substrate materials as a function of the light incidence angle for p-polarized radiation (solid lines) and s-polarized radiation (broken lines) at 3000 cm⁻¹. A hypothetical adsorbate vibration (absorption index k=0.1 at 3000 cm⁻¹) of an isotropic adsorbate layer (thickness d=1 nm, refractive index n=1.5) was used to simulate a CH-stretching absorption in an organic monolayer film. The following optical constants were used for the substrates: silicon (n=3.42, k=0), glass (n=1.5, k=0), gold (n=3, k=30). ϑ_B denotes the Brewster angle of the substrate. (Figure taken from Ref.^[94]).

The basic design of the IRRAS is illustrated in Fig. 2.8. The path of the IR beam is shown as a yellow bold line in the figure. The figure has four main components, namely, an IR beam source (laser diode), interferometer, sample holder, and detector compartment.



Figure 2.8 Schematic of an IRRAS instrument. (Figure taken from Ref.^[95])

In this thesis, all samples were recorded using an FTIR spectrometer (Bruker VERTEX 80) with a resolution of 2 cm⁻¹ at an incidence angle of 80° relative to the surface normal. Liquid nitrogen is used to cool the mercury cadmium telluride (MCT) narrow band (4000–400 cm⁻¹) detector. Dry air was purged continuously through the spectrometer and sample compartment, which reduces the possibility of atmospheric water or CO_2 contamination on the samples. Samples were measured as long as the water absorption bands from ambient air disappeared (900–1300 scans). The data were processed using Bruker OPUS[®] software version 7.2.

2.2.4 Attenuated total reflection

ATR is a very simple and effective IR spectroscopy technique used to characterize samples directly in the solid or liquid state without further preparation.

ATR technique detects the total internal reflection resulting from an evanescent wave produced by an IR beam passed through the ATR crystal at least once off the internal surface in contact with the sample (Fig. 2.8). The penetration depth (d_p) into the sample is typically between 0.5 and 2 µm, with the exact value determined by the wavelength of light, angle of incidence, indices of refraction for the ATR crystal, and the medium being probed. Different numbers of reflections can be obtained by altering the angle of incidence. The following conditions should be satisfied with the ATR technique: the sample must be in contact with the ATR crystal surface and the refractive index of the layer must be smaller than that of the ATR crystal.



Figure 2.9 Schematic of attenuated total reflection (Figure taken from Ref.^[96]).

In this thesis, all samples were recorded using a Bruker Optics Tensor 27 spectrometer with a Bruker Optics Platinum[®] ATR accessory and a duterated triglycine sulfate detector. The ATR spectra were recorded at room temperature with a resolution of 4 cm⁻¹ using air as background. Data were processed using Bruker evaluation software OPUS 7.2.

2.3 Raman spectroscopy

Raman spectroscopy is commonly used in chemistry to provide a fingerprint of chemical bonds in sample by observing the vibrational, rotational, and other low-frequency modes in a system. This fingerprint was first observed by Sir C. V. Raman in 1928. Raman spectroscopy is a good complement to IR absorption spectroscopy because it can measure molecules or bonds that have no dipole moments (IR inactive), such as N_2 and O_2 .

The basic rationale of Raman spectroscopy is described using classical arguments. A schematic of the basic mathematical description of the Raman effect is shown in Fig. 2.10. The electromagnetic field will perturb the charged particles of the molecule, resulting in an induced dipole moment, as follows:

$$\mu = \alpha E \tag{4}$$

where α is the polarizability, *E* is the incident electric field, and μ is the induced dipole moment. The electric field of the radiation is oscillating as a function of time at a frequency V_0 , which can induce an oscillation of the dipole moment μ of the molecule at this same frequency (Fig. 2.10a). The polarizability α of the molecule has a certain magnitude that can vary slightly with time at the much lower molecular vibrational frequency V_m (Fig. 2.10b). The results are shown in Fig. 2.10c, which depicts an amplitude modulation of the dipole moment oscillation of the molecule. This type of modulated wave can be resolved mathematically into three steady amplitude components with frequencies V_0 , $V_0 + V_m$, and $V_0 - V_m$ (Fig. 2.10d). These dipole moment oscillations of the molecule can emit scattered radiation at the same frequencies called Rayleigh, Raman anti-Stokes, and Raman Stokes frequencies. If a molecular vibration does not cause a variation in the polarizability, then no amplitude modulation of the dipole moment oscillation would occur and no Raman Stokes or anti-Stokes emission would be observed.



Figure 2.10 Schematic representing Rayleigh and Raman scattering. In (a). the incident radiation makes the induced dipole moment of the molecule oscillate at the photon frequency. In (b), the molecular vibration can change the polarizability, a, which changes the amplitude of the dipole moment oscillation. The result as shown in (c) is an amplitude modulated dipole moment oscillation. The image (d) shows the components with steady amplitudes which can emit electromagnetic radiation (Figure taken from Ref.^[93]).

In this thesis, the Raman spectra were recorded with a Bruker Senterra Raman microscope (Bruker Optics, Ettlingen, Germany) using a green laser at 532 nm for excitation. Data were processed using Bruker evaluation software OPUS 7.2.

2.4 Ultraviolet–visible spectroscopy

Ultraviolet–visible spectroscopy (UV-Vis) is one of the most widely used analytical methods to obtain absorbance or reflectance spectroscopy of materials in the UV-vis spectral region. Samples for UV-vis spectroscopy are most often liquids, although the absorbance of gases and even of solids can also be measured. This technique is complementary to fluorescence spectroscopy.

The energy irradiated on the molecules can induce changes in the electronic nature between ground and excited states. The electrons in a molecule can be divided into three types: σ (single bond), π (multiple-bond), or non-bonding (n-caused by lone pairs) electrons. These electrons, when absorbing energy in the form of light radiation, become excited from the highest occupied molecular orbital (HOMO) to the lowest unoccupied molecular orbital (LUMO). The resulting species is known as the excited state or anti-bonding state (Fig. 2.11).

1. The σ -bond electrons are located at the lowest energy level and require much energy to be excited into higher energy levels. Consequently, these electrons absorb light in the lower wavelengths of the UV light.

2. The π -bond electrons are located at much higher energy levels for the ground state and are relatively unstable. Thus, they can be excited by lower energy. These electrons absorb energy in the UV and visible light radiations.

3. Non-bonding electrons belong to lone pairs of atoms. They are at higher energy levels than π -electrons and can be excited by UV or visible light.



Figure 2.11 Different transitions between the bonding and anti-bonding electronic states when light energy is absorbed in UV visible spectroscopy.

The basic design of the UV-Vis is illustrated in Fig. 2.12. The path of light is shown as a green bold line at the bottom of the figure. In a typical double-beam instrument, the light is split into two beams before it reaches the sample. One beam is used as the reference (the intensity is considered as 100% transmission or 0% absorbance), whereas the other beam passes through the sample (the measurement displayed is the ratio of the two beam intensities).



Figure 2.12 Schematic of UV-vis spectroscopy (Figure taken from Ref.^[97]).

In this thesis, the UV-vis spectra were recorded by a Cary 5000 spectrophotometer (Agilent Technologies) in transmission mode using a quartz glass substrate.

Dynamic UV-Vis spectra were recorded by an Optics unit, a temperature control unit, $XNano^{TM}$ measurement cell, and $X1^{TM}$ high temperature reactor (Insplorer[®]). All Insplorion systems were delivered with a personal computer with Windows platform and pre-installed control software Insplorer[®].

2.5 X-ray photoelectron spectroscopy

X-ray photoelectron spectroscopy (XPS) is the most widely used surface-sensitive quantitative spectroscopic technique, which was developed by Kai Siegbahn in 1954. The first commercial monochromatic XPS instrument was produced in 1969. It can be used to measure elemental composition, empirical formula, chemical state, and electronic state of elements that exist within a material.

XPS spectra are obtained by measuring the kinetic energy and number of electrons that escape from the top 0 nm to 10 nm of the material by irradiating a material with a beam of X-rays. The XPS apparatus has four main components, namely, a source of focused X-ray beam, sample holder, electron detector, and an ultra-high vacuum (UHV) stainless steel chamber equipped with UHV pumps (Fig. 2.13).



Figure 2.13 Schematic of the XPS system (Figure taken from Ref.^[98]).

When the incident X-ray irradiates the sample surface, an atom or molecule will absorb the X-ray and an electron can be ejected. The kinetic energy (E_{κ}) of the

electron depends upon the photon (hv) and binding (E_B) energies of the electron. The relationship is given in the following equation:

$$E_k = hv - E_B - \Phi \tag{5}$$

where Φ is the work function dependent on both the spectrometer and the material. The typical chemical states and binding energy of the elements on the surface of material can be determined by measuring the kinetic energy of the emitted electrons.

In this thesis, the XPS measurements were performed on a K-alpha spectrometer (ThermoFisher Scientific, East Grinstead, UK) using a microfocused, monochromated Al K α X-ray source (400 μ m spot size).

2.6 Electrospray Ionization Mass Spectrometry

Electrospray ionization mass spectrometry (ESI-MS) is a soft ionization technique that is typically used to determine the molecular weights of solid or liquid samples. This technique allows the sample to be nonvolatile or thermally unstable. This characteristic indicates that ionization of samples, such as organic and inorganic molecules, can be performed, but a molecule with a fairly large mass (normally over 100) is required. The other major disadvantage is that the sample should be well dispersed in a solution.

The ESI-MS experiments are conducted by detecting the ratios of mass to charge of various peaks in the spectrum. Initially, the ions in solution are ionized into small droplets. Subsequently, these droplets will be further desolvated into even smaller droplets to create molecules with attached protons. Finally, these ionized and desolvated molecular ions will be passed through the mass analyzer to the detector, and the mass of the sample can be determined (Fig. 2.14).



Figure 2.14 Schematic illustration of the electrospray ionization mass spectrometry. (Figure taken from Ref.^[99]*)*

In this thesis, ESI-MS was acquired with a Bruker micro OTOF-Q II spectrometry. The scan range was m/z 50–1500 under dry gas-nitrogen at 120 °C.

2.7 Inductively coupled plasma atomic emission spectroscopy

Inductively coupled plasma atomic emission spectroscopy (ICP-OES) is an analytical technique used for the detection of trace metals in solution (mostly water-dissolved). This technique become widely applied in both routine research and in more specific analysis purposes because of its reliability, multi-element options, and high throughput. This technique has been commercially available since 1974. It uses the inductively coupled plasma to produce excited atoms and ions that emit electromagnetic radiation at wavelengths characteristic of a particular element.

ICP-OES can monitor all metal elements and few nonmetal elements (e.g., O, F, and N) (Fig. 2.15). ICP-OES can readily measure compositions at parts per million (mg/L) concentration level and with the axial systems up to parts per billion (μ g/L) concentration levels can be reached compared with other conventional analytical methods. The major disadvantage of this method is that the solid sample should first be dissolved into acid solution during sample preparation. In addition, samples should not contain any organic solvents.



Figure 2.15 Elements available for analysis by the optima 70000DV inductively coupled plasma atomic emission spectrometer. (Figure taken from Ref.^[100]).

ICP-OES was performed using a Perkin-Elmer model Optima 8300 DV equipped with a GemTipTM Crossflow Nebulizer (Perkin Elmer, USA). All samples used in this work were dissolved with an acid solution (65% nitric acid), and the concentration of sample solution in the liquid nitric acid was higher than 0.00X mg/L.

2.8 Time-of-flight secondary ion mass spectrometry

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) is a surface analytical technique, which was developed by Herzog and Viehböck in 1940s. ^[101] A pulsed beam of primary ions is focused onto a sample surface, producing secondary ions in a sputtering process. These secondary ions are analyzed to provide information on the molecular and elemental species presented on the surface (Fig. 2.16). ToF-SIMS is a conventional technique that can detect all elements in the periodic table, including hydrogen. Moreover, ToF-SIMS can provide not only the mass spectral information of the sample with XY dimension but also the depth profile information on the Z dimension.



Figure 2.16 Schematic of the time-of-flight secondary ion mass spectrometry. (Tof-SIMS) (Figure taken from Ref.^[101]*)*

The ToF-SIMS measurements were performed on a ToF-SIMS 5 instrument (ION-ToF GmbH, Münster, Germany). A 20 keV C_{60}^+ ion beam with a short pulse width (2 ns) was applied as analysis beam in all experiments. For quasi-static SIMS, this beam was rastered over 500 × 500 μ m², and dose density was limited to below 1011 ions/cm² (static limit). For dynamic SIMS, an additional O²⁺ beam (500 eV) was applied for erosion of a 450 × 450 μ m² field with a concentric analysis field of 250 × 250 μ m². Spectral calibration was performed on C, Cu, Bi, and Bi₃O₄ peaks. Mass deviations were below 20 ppm.

2.9 Scanning electron microscope

SEM is a type of electron microscopy that displays a 2D image of the sample using a focused beam of electrons that scan the sample surface. The first high-magnification scanning electron microscope was invented by Ardenen in 1937.

A typical SEM apparatus is shown in Fig. 2.17, in which a high-energy focused electron beam interacts with atoms in the sample, producing various signals with information on the surface topography and composition of the sample. The resolution of the SEM images can achieve a value better than 1 nm. Samples can be observed in high or low vacuum under wet conditions (in environmental SEM) and at a wide range of cryogenic or elevated temperatures.



Figure 2.17 Schematic of an scanning electron microscope.(*Figure taken from Ref.*^[102]).

All samples, including SEM cross-sectional measurements, were analyzed using a Zeiss HR-SEM (Gemini Class) at 3–5 kV to check the continuity, compactness, and homogeneity of differently prepared (loaded and unloaded) HKUST-1 SURMOF thin films.

2.10 Atomic force microscopy

AFM is a high-resolution scanning probe microscopy, which was invented by IBM scientists in 1986. Compared with the SEM, AFM can be applied to acquire morphological information of a sample surface with 3D detail in air or liquid environment. This technique had been widely used in materials science, biology, and other fields since its inception.

The basic design of the AFM illustrated in Fig. 2.18 shows the four main components, namely, sample stage, AFM cantilever, laser, and 4-quadrant photo detector. The top of the AFM cantilever contains a sharp tip (probe), which is used to scan the specimen surface. When the tip is brought near a sample surface, forces between the tip and the sample surface lead to a deflection of the cantilever according to Hooke's law.^[103] The deflection of the cantilever was monitored by a four-quadrant photo detector by receiving a reflected laser signal from the back of the cantilever. Finally, the morphologies of the sample in the x-, y-, and z-directions were recorded

and rendered as a 3D image.



Figure 2.18 Schematic of an atomic force microscope. (Figure taken from Ref.^[104]).

In this thesis, AFM measurements were performed using an Asylum Research Atomic Force Microscope, MFP-3D BIO. All experiments were operated in air at 25 °C. AFM cantilevers were NSC-18 AFM-HQ and were purchased from NanoAndMore, with a nominal resonance frequency (75 kHz) and nominal spring constant (3.5 N/m).

2.11 Transmission electron microscopy

TEM is a microscopy technique in which a beam of electrons is transmitted through an ultra-thin specimen, interacting with the specimen as it passes through. The first transmission electron microscope was built by Max Knoll and Ernst Ruska in 1931. This microscope had a resolution higher than that of light in 1933. The first commercial transmission electron microscope was released in 1939.

TEM has become a major analytical method in various scientific fields, in both physical and biological sciences. This technique can be applied in cancer research, virology, and materials science, as well as in pollution, nanotechnology, and semiconductor. TEM image contrast at low magnification is due to the absorption of electrons in the material caused by the thickness and compositional variations in the material. Complex wave interactions at high magnification modulate the intensity of the image, requiring expert analysis of observed images. Alternate modes of use facilitate the observation of modulations in chemical identity, crystal orientation, electronic structure, and sample-induced electron phase shift, as well as the regular absorption-based imaging.

The basic design of a transmission electron microscope, illustrated in Fig. 2.19, consists of four key parts, namely, the electron source, electromagnetic lens system, a sample holder, and an imaging system. A transmission electron microscope works similar to a slide projector. A projector shines a beam of light, which transmits through the slide. The patterns painted on the slide allow only certain parts of the light beam to pass through. Thus, the transmitted beam replicates the patterns on the slide, forming an enlarged image of the slide when falling on the screen. TEM works similarly except that they shine a beam of electrons (similar to the light in a slide projector) through the specimen (similar to the slide). However, the transmission of electron beam in TEM is highly dependent on the properties of the material being examined, such as density and composition. For example, porous materials will allow more electrons to pass through, whereas dense materials will allow less. Consequently, a specimen with non-uniform density can be examined by this technique. The transmitted beam is projected onto a phosphor display.



Figure 2.19 Schematic of a transmission electron microscope. (Figure taken from Ref.^[105]).

In this work, the plane-view TEM measurements were performed using an image aberration-corrected FEI Titan 80-300 operated at 300 kV and equipped with a Gatan US1000 CCD camera for TEM and SAED analysis and a Fischione HAADF detector for STEM imaging. An EDAX S-UTW detector was used for X-ray energy dispersive

microanalysis (EDX) analysis. SAED and STEM analyses were performed at LN_2 temperatures to reduce electron beam damage of the sample. The samples were prepared by removing the Bi₂O₃@HKUST-1 thin films from quartz-glass sample surface through a laser ablation process and transferred onto a holey carbon Au grid (Quantifoil GmbH).

2.12 Quartz crystal microbalance

The QCM device measures the mass variation per unit area on the surface of a quartz crystal resonator by monitoring the change in frequency. This resonance frequency is achieved by the addition or removal of a small mass from the surface of the QCM sensor. The QCM has been commonly used as a micro-gravimeter since Sauerbray reported a linear relationship between the oscillation frequency of a piezoelectric crystal and the mass of a bound film in 1959. The QCM can be used under vacuum, gas, and liquid environments, at temperatures between 20 °C to 60 °C, achieving nanogram mass precision.

The basic design of the QCM is illustrated in Fig. 2.20. The device consists of a thin quartz disc sandwiched between a pair of electrodes, which can be excited to oscillate at its resonance frequency by the application of an alternating voltage. The resonance frequency depends on the total oscillating mass of the sensor and sensor surface monolayer, such as absorbed solvent. Thus, the QCM operates as a very sensitive balance that can be used for monitoring the change in mass of a sample.



Figure 2.20 Schematic of a piezoelectric quartz crystal microbalance (QCM) crystal (only one side shown). A typical 5 MHz QCM from International Crystal Manufacturing consists of a thin quartz crystal (0.85 cm diameter) sputtered with a metal electrode (0.35 cm diameter) on each side. (Figure taken from Ref.^[106]).

In this thesis, QCM was employed to monitor the growth of an SURMOF thin film on

a QCM sensor in a clean and well-controlled manner. The QCM sensor was placed in a flow cell (Q-Sense E4). Infiltration with guest molecules was achieved via a stream of liquid through the cell. The QCM sensors consist of a quartz glass which is cover on both sides with gold electrode (see Fig. 2.20). All SURMOF samples used in this work were grown directly on MHDA or MUD SAM modified gold QCM sensors. The SURMOF growth was performed in situ in a QCM flow cell by alternating between a metal source solution, and a solution of ligand in ethanol and pure ethanol as described previously.^[107]

2.13 Electrochemistry at semiconductor electrodes

Measurements of the electrode properties of semiconductors can provide information on the properties of the sample (such as E_{CS} , E_{VS} , Fermi energy, surface barrier, and density of majority carriers) and possible electron transfer occurring during the reactions. Numerous experimental results in a previous study have been provided to support the behavior of MOFs as semiconductors.^[108, 109] Therefore, measurements of the semiconductor electrochemistry of MOF-basic samples are crucial to understand the architecture and behavior of the materials.

The simplest method to investigate a semiconductor electrode is the measurement of electrode capacity. Capacity measurements indicate the value of the surface barrier (V_s), which controls the density n_s or p_s , the key parameters in determining the electrode current. In addition, the energy level E_{CS} or E_{VS} can also be determined using capacity measurements. A simple circuit for impedance measurement is illustrated in Fig. 2.21. The typical three-electrode system used in this method includes a working electrode (connect with sample), a counter electrode (platinum, Pt), and a reference electrode (silver/silver chloride, Ag/AgCl).



Figure 2.21 Schematic of cell featuring impedance measurement (Figure taken from

Ref.^[110]).

A Mott–Schottky plot using the following generalized equation can be determined by measuring the semiconductor electrode capacity as a function of the direct current–applied voltage.

$$N_a = (2/e_0 \varepsilon \varepsilon_0) \left[d\left(1/C^2\right)/dV \right]^{-1}$$
(6)

where e_0 is the electron charge, ε is the electrode dielectric constant, ε_0 is the vacuum permittivity and N_{α} is the acceptor density.

Two important parameters are determined from the C/V data using equation (5), namely, the flatband potential E_{fb} (extrapolation from the depletion layer region of voltages to the intercept) and the density of charge in the space charge region N_{sc} . In addition, the type of the semiconductor can be determined by the Mott–Schottky plot. An upcurve indicates a semiconductor with n-type behavior and a declining curve means the semiconductor with p-type behavior (Fig. 2.22).



Figure 2.22 Typical Mott-Schottky plot of C^2 versus electrode potential (Figure taken from Ref.^[110]).

In this thesis, Mott–Schottky measurements were performed using an electrochemical workstation (CAMRY, reference 600) with a three-electrode setup, including a platinum counter electrode and a Ag/AgCl reference electrode (saturated KCl solution).

3 Materials and theoretical analysis

3.1 Materials

3.1.1 Substrates

Silicon substrates were purchased from Silicon Sense (US) for general use (Thickness: 525 \pm 20 μ m; specific resistivity: 8-12 Ω /cm).

Gold substrates were purchased from Georg Albert–Physical Vapor Deposition (Silz, Germany) (100 nm Au + 5 nm Ti evaporated on Si substrates).

Quartz glass were purchased from Hellma Optics GmbH Jena (Germany) (Ø 10 mm, Thickness: 0.5 mm – 1.0 mm, Delay: $\lambda/4$, $\lambda/2$, Wavelength range: 180 – 2700 nm).

3.1.2 Chemicals

16-mercaptohexadecanoic acid (MHDA, 99%, Aldrich) 11-mercapto-1-undecanol (MUD, 99%, Aldrich) 4-(4-pyridyl)phenyl)-methanethiol (PP1, 99%) 1,3,5-benzenetricarboxylic acid (BTC, Sigma-Aldrich) Copper (II) acetate hydrate (Cu(OAc), 98%, Sigma-Aldrich) Terephthalic acid (BDC, 99%, Sigma-Aldrich) 2,5-bis-(allylthio)-terephthalic acid (atBDC, 99%) 2,5-bis-(allyloxy)-terephthalic acid (aoBDC, 99%) 1,4-diazabicyclo[2.2.2]octane (dabco, 99%) Lanthanum(III) trifluoromethanesulfonate (La(OTf)₃, Sigma-Aldrich) Nuclear fast red (NFR, 99%, Sigma-Aldrich) Triphenylbismuth (BiPh₃, 99%) Chlorocarbonyl gold, (AuClCO, 99%, Sigma-Aldrich) Ethanol (99.99%, VWR) Acetic acid (100%, VWR) Hydrochloride (37%, in water, VWR) Sulfuric acid (≥95%, VWR) Dichloromethane (≥99.8, VWR)

3.2 SAM preparation on Au substrates

The 16-mercaptohexadecanoic acid (MHDA, 99%, Aldrich) solution was prepared by dissolving MHDA in a 5% (by volume) solution of acetic acid in ethanol (VWR) to reach the desired concentration of 20 μ M. A clean gold substrate was placed in this solution for 72 h and then rinsed with the pure solvent and gently dried under nitrogen flux (see Fig. 3.1).



Figure 3.1 Schematic of MHDA SAM on gold wafer.

The 11-mercapto-1-undecanol (MUD, 99%, Aldrich) solution was prepared by dissolving MUD in ethanol (VWR) to reach the desired concentration of 1 mM. A clean gold substrate was placed in this solution for 24 h and then rinsed with the pure solvent and gently dried under nitrogen flux (see Fig. 3.2).



Figure 3.2 Schematic of MUD SAM on gold wafer.

The 4-(4-pyridyl)phenyl)-methanethiol (PP1, 99%) solution was prepared by dissolving PP1 in ethanol (VWR) to reach the desired concentration of 1 mM. A clean gold substrate was placed in this solution for 1 h (60 $^{\circ}$ C) and then rinsed with the

pure solvent and gently dried under nitrogen flux (see Fig. 3.3).



Figure 3.3 Schematic of PP1 SAM on gold wafer.

3.3 Surface treatment of other substrates

Chemical or physical processes can be used to treat the surface of silicon substrate and quartz glass. In the chemical process (Fig. 3.4), the substrates were initially immersed in a mixture of H_2SO_4/H_2O_2 (3:1) for at least 30 min. Then, the samples were removed from solution, rinsed with pure ethanol, and finally dried in a flux of N_2 gas. This treatment resulted in a silicon substrate or quartz glass surface has a link with -OH groups. A substrate functionalized with -COOH group was obtained using the 11-(trie-thoxysilyl)-undecanal chemical to modify -COH group on the -OH functionalized substrate at room temperature for 3 h. Subsequently, the substrate with -COH group was oxidized by potassium hypermanganate (0.1 mol/L) for 1 h to obtain -COOH functional group.^[74, 111]



Figure 3.4 Schematic of preparation of –OH and –COOH functionalized groups on silicon substrate and quartz glass by chemical process (Figure change from Ref.^[111]).

A second method, we expose the substrate to the O_2 plasma which is able to graft -OH groups onto the substrate surfaces. The plasma is created by using high frequency voltages (kHz to MHz) to ionize the low pressure oxygen (around 1 mbar). In this plasma cleaning process, the substrates were initially put in oxygen plasma environment for at least 30 min. Subsequently, the samples were taken out from machine, rinsed with pure ethanol, and finally dried in a flux of N_2 gas. The OH functional groups were directly grown onto the substrate surfaces.^[112]

3.4 Theoretical analysis

Theoretical analysis was contributed by Tobias Neumann, Dr. Denis Danilov and Prof. Wolfgang Wenzel from Institute of Nanotechnologie (INT), Karlsruhe Institute of Technology.

DFT calculations of loading La³⁺ ionic compound into HKUST-1 SURMOFs

In this thesis, molecular modelling simulations were performed by using a Monte Carlo algorithm implemented in the simulation package SIMONA.^[113] Basing hopping approach with consecutive simulated annealing cycles was used to obtain the lowest energy for the system. Therefore, we can avoid the trapping of the system in metastable conformations. ^[114-116] Each simulated annealing cycle consists of Metropolis Monte Carlo steps is start at high temperature, so that the molecule can overcome local minimal and traverse energy barriers. The ambient temperature is decreased by following expression:

$$T_n = T_s \cdot c^n, \quad c = \left(\frac{T_E}{T_s}\right)^{\frac{1}{N}} < 1 \tag{1}$$

where T_n is the temperature at step n, T_s is the temperature in the end and N is the total number of steps in simulated annealing run.

The interaction between the atoms can be expressed by the classical electrostatic potential:

$$\Phi(\vec{r}_i) = \frac{1}{4\pi\varepsilon\varepsilon_0} \sum_{j}^{N_B} \frac{q_i}{r_{ij}}$$
(2)

and the Lennard-Jones interaction that includes terms accounting for van-der-Walls attraction and Pauli repulsion:

$$U_{LJ}(r) = \sum_{i}^{N_A} \sum_{j}^{N_B} 4\mathcal{E}_{ij} \left(\left(\frac{\sigma_{ij}}{r_{ij}} \right)^{12} - \left(\frac{\sigma_{ij}}{r_{ij}} \right)^6 \right)$$
(3)

Standard parameters for the Lennard-Jones interaction were used for all atoms except La^{3+} . In order to determine the LJ parameters for La^{3+} , we performed

Metropolis Monte Carlo simulations of La^{3+} with 3 OTf at constant low temperature (T=1K). At the same time, we need varied the La-parameters until the distance between oxygen and La^{3+} reached the equilibrium distance obtained from ab-initio calculations. The resulting parameters for La^{3+} are epsilon = 0.15kcal/mol and sigma = 3.425Å. Partial charges were calculated using the ESP fit implemented in the DFT code TURBOMOLE ^[117] using SV(P) basis and b3-lyp functional (see Fig. 3.4).



Figure 3.4 Calculation of partial charges of the HKUST-1 MOF.

We were constructed to screen possible configurations a system consisting of two neighboring cavities (the middle and large cavities of the HKUST-1). Each cavity was loaded with up to 4 $La(OTf)_3$ molecules resulting in 24 different model systems. We applied a strong restraining force to particles outside the cavities which to prevent the ions from leaving the complex:

$$U_{confine}(q) = k(q - x_o)^2, q > x_0 \text{ or } q < -x_0, q = x, y, z$$
(4)

The simulations consisted of 10 simulated annealing runs with N = 100000 Metropolis Monte-Carlo steps each, starting at Ts = 750K and ending at TE = 300K using rigid body translation for La³⁺ and (OTf) and in addition rigid body rotation and rotation around dihedral angles in the (OTf) ions. The step size for the random rigid translations was drawn from a random uniform distribution between 0 and 1Å, the angle of the rigid rotations from a random uniform distribution between 0° and 180°.

DFT calculations of loading Bi³⁺ ionic compound into HKUST-1 SURMOFs are similar to the above modeling approaches.

4 Loading metal ions into SURMOFs by using benzene ring as nucleation centers

One of the most popular strategies of loading metal ions into SURMOF is using immersion process. In this method, the SURMOF samples are directly immersed into metal precursor solutions. The metal ions will enter and be adsorbed on the phenyl ligands. The results demonstrate that this method is rapid and effective for loading metal ions into SURMOFs. However, the number and locations of the metal ions within MOFs are hard to be determined because they are loaded randomly. In addition, usually, the adsorption capacity between the benzene ring and metal ions is rather low, which will limit the number of metal ions loaded into MOF.

4.1 Loading of La³⁺ ionic compounds into HKUST-1 SURMOFs

Here, we present the results of a combined theoretical and experimental study on the loading of La³⁺ ionic compounds into HKUST-1 SURMOFs by using phenyl ligands as nucleation centers.

4.1.1 Background

MOFs have become one of the most important carriers in highly porous crystalline materials due to their flexible pore sizes and large loading capacity for guest species, in particular metals and metal ions. During the past decade, a huge number of metal@MOF systems (such as Au,^[118] Zn,^[119] Pd^[120]) have been reported, with the metal guests rendering fascinating properties (e.g., such as hydrogen storage,^[121, 122] CO oxidation,^[79, 123] alcohol oxidation^[124]) to the host MOF materials. However, the characterization of metal ions loaded MOF materials is a major challenge, because it is hard to show the distribution of metal ions in the lattice of MOFs. That is, the usual visible characterization methods (such as TEM, SEM) show only the agglomerates or nanoparticles of metal ions but it's incapable of monitoring monodispersed metal ions.

In this work, we investigate the La^{3+} species, $La(OTf)_3$ (chemical structural formula shown in Fig. 4.1.1b), loaded into HKUST-1 or $Cu_3(BTC)_2$ (Fig. 4.1.1). The experiments were carried out by using the structure platform provided by HKUST-1, a classical of metal organic frameworks with fairly large (~1 nm) pore sizes (Fig. 4.1.1a).^[21] Investigations were carried out using theoretical and experimental XRD, and quantitative information on the Cu/La-ratio is obtained from ICP-OES and XPS. The force-field calculations were carried out to obtain the precise positions of the metal ions in the lattice.



Figure 4.1.1 (a) Schematic structure of HKUST-1. (b) Schematic structure of HKUST-1 SURMOF grown on a MHDA SAM after loading La(OTf)₃.

4.1.2 Preparation of the La(OTf)₃@HKUST-1 SURMOF

HKUST-1 SURMOFs were grown on modified Au substrates using the spray method, as described in more detail in section 1.3.2.1. In this experiment, the HKUST-1 SURMOFs were grown on an Au substrate functionalized by COOH-terminated SAM. Before further experiments, all SURMOF samples were activated by ultrasound in dichloromethane solution for 5 min to remove residual solvent from the SURMOF pores and finally checked by XRD.

The preparation of La(OTf)₃@HKUST-1 SURMOF was performed by using the immersion method. A HKUST-1 SURMOF was put into a 250 ml flask and then evacuated to 0.2 kPa at room temperature for 30 min. Subsequently, the sample was immersed in a freshly prepared solution of La(OTf)₃ in ethanol (1 mM, Aldrich) kept at 65 °C (Fig. 4.1.2). And last, an immersion time of 12 h the sample was removed from the solution, rinsed with pure ethanol, and finally dried in a flux of N₂ gas. After loading experiment, all loaded samples were characterized by XRD before further measurements.



Figure 4.1.2 Synthesis scheme of gas-phase loading method.

4.1.3 Results and discussion

4.1.3.1 Morphology analysis of the HKUST-1 SURMOF by AFM and SEM

The morphologies of HKUST-1 thin film were characterized by SEM (Fig. 4.1.3) and AFM (Fig. 4.1.4). It clearly shows that continuous and homogenous HKUST-1 MOF thin films were successfully synthesized on the gold surface by MHDA-SAM surface modification (Fig. 4.1.3 right). The thickness of SURMOFs is about 100 nm by calculation from cross-section SEM picture (Fig. 4.1.3 left). The AFM images also confirmed the HKUST-1 MOF thin film is continuous and homogenous (Fig. 4.1.4).



Figure 4.1.3 SEM images of 20 cycles of HKUST-1 SURMOF.



Figure 4.1.4 AFM images of 20 cycles of HKUST-1 SURMOF.

4.1.3.2 IR analysis of the samples obtained before and after La(OTf)₃ loading

The result obtained from the IR is shown in Fig. 4.1.5. The presence of a broad and strong band at 1700–1300 cm⁻¹ is assigned to vibrations of COO- of pristine HKUST-1 [1655 cm⁻¹ (COO- asymmetric stretching), 1457 cm⁻¹ (COO- symmetric stretching) and 1388 cm⁻¹ (COO⁻ symmetric stretching)] (Fig. 4.1.5 black curve). These data agree well with those reported previously for pristine HKUST-1.^[125] The characteristic absorption bands of pristine HKUST-1 SURMOF are summarized in table 4.1.1.



Figure 4.1.5 IR spectroscopy of 20 cycles of HKUST-1 SURMOF (black) and after loading $La(OTf)_3$ (red).

Absorption band (cm ⁻¹)	Assignment		
1654 and 1595	(COO ⁻) asymm. Stretching		
1455 and 1383	(COO ⁻) symm. Stretching		
1112	aromatic C-H ip.		
941	aromatic C-H oop.		

Table 4.1.1 Band assignment for the IR spectrum of HKUST-1 on MHDA SAM.

After immersing the HKUST-1 SURMOFs in a La(OTf)₃ solution, a new characteristic R-SO₃ vibration at 1042 cm⁻¹ has appeared (Fig. 4.1.5 red curve). This observation provides strong support that the (OTf) anion is adsorbed in the SURMOFs. Therefore, we believe that the La³⁺ ions are loaded into the SURMOFs. Also after loading the IR bands of the samples do not show significant changes, suggesting that the structure of HKUST-1 remains intact. The loading of La(OTf)₃ does not break the framework of HKUST-1 SURMOF.

4.1.3.3 XRD analysis of the samples obtained before and after La(OTf)₃ loading

According to the XRD data (Fig. 4.1.6 black), the sharp well-defined (002) and (004) peaks are observed in out-of-plane XRD for the pristine HKUST-1 SURMOFs. This demonstrates that SURMOF growth proceeds only along the (001) direction on the MHDA SAM. This result was fit well with the reported results in the previous work.^[74] The relative intensity of (002)/(004) for the pristine HKUST-1 SURMOFs agrees with that observed for MOF powders obtained from simulations using the well-established bulk structure of HKSUST-1. In addition, the in-plane XRD data showing only the (200) and (220) directions also support this orientation structure (Fig. 4.1.6, red).

After immersing sample into the La(OTf)₃ solution, the recorded XRD data are shown in Fig. 4.1.6 (out-of-plane, blue; in-plane, dark yellow). The periodicity of the MOF crystal lattice has remained unchanged because there has no new diffraction peaks appeared. However, the form factor is very different. The ratio of (002)/(004) has decreased from 1.1 (pristine sample) to 0.7 (loaded sample). And also, the ratio of (200)/(400) and (220)/(440) has dropped from 1.6 to 0.1 and 2.7 to 0.8, respectively. Longer immersion times did not lead to a further change of the relative XRD peak intensities. This significant change in relative peak intensities are demonstrating that La³⁺ ions are loaded into the larger and middle pores of the HKUST-1, a gather of the outer MOF surface would not be compatible with the change of diffraction relative peak intensities. The same loading process has also been carried out for powder HKUST-1: the changes in relative peak intensities were similar to the SURMOFs (Fig. 4.1.7): after loading La(OTf)₃, the ratio of (002)/(004) has dropped from 2.15 to 1.21.



Figure 4.1.6 XRD patterns recorded: calculated XRD patterns for HKUST-1 with a bulk structure (purple) and experimental XRD data recorded in out-of-plane [empty HKUST-1 (black) and after loading $La(OTf)_3$ (blue)] and in-plane [empty HKUST-1 (red) and after loading $La(OTf)_3$ (dark yellow)] scattering geometry.



Figure 4.1.7 XRD patterns of bulk HKUST-1 MOF (black), after loading $La(OTf)_3$ (red) and calculated data(blue).

4.1.3.4 Stability of the La(OTf)₃@HKSUT-1 SURMOF studied by XRD

The out-of-plane XRD was applied to investigate the stability of the $La(OTf)_3@HKSUT-1$ SURMOF after immersion in dichloromethane under ultrasonic conditions for 15 min. The XRD data (Fig. 4.1.8) do not show significant changes suggesting an irreversible loading of the SURMOF with $La(OTf)_3$. Also we do not see significant changes of the position as well as on the relative intensities of the peaks. This demonstrates that the La^{3+} ions do not leach out after loaded inside the cavity of HKUST-1 when immersed in solvents like CCl_2H_2 .



Figure 4.1.8 XRD patterns of La(OTf)₃@HKUST-1 SURMOF (black) and after ultrasonic cleaning in dichloromethane for 15min

4.1.3.5 Quantitative analysis by XPS and ICP-OES

In order to obtain detailed information about the number of the molecules within the MOF pores, we measured the $La(OTf)_3@HKSUT-1$ SURMOF using XPS and ICO-OES.

In contrast to powder MOFs, XPS can be better applied to SURMOFs supported on a metal because it avoids electrical charging which greatly complicates the data interpretation. Clearly, after loading the data recorded for the La(OTf)₃@HKUST-1 SURMOFs show distinctive La³⁺ peaks (Fig. 4.1.9).^[126] A quantitative analysis reveals that the total Cu²⁺ and La³⁺ contents of the SURMOFs after loading are 4.3% and 0.8%, respectively (Table 4.1.2), corresponding to a Cu/La ratio of 5.4.

The metal ion concentration curves obtained from ICP-OES are shown in Fig. 4.1.10.
By calculation of the integrated area of the measured curves, the Cu^{2+} and La^{3+} concentrations after loading the sample are 6.6 mg·L⁻¹ and 0.9 mg·L⁻¹, respectively. The calculated ratio of Cu/La amounts to 7.3, which is close to the value calculated from XPS data (Table 4.1.3).



Figure 4.1.9 XPS analysis of (a) Cu 2p and (b) La 3d of the La(OTf)₃@HKUST-1 MOF thin films.

Table 4.1.2 Element composition determined by XPS analysis for La(OTf)₃@HKUST-1 SURMOF.

Name	Amount %	Cu/La ratio
La ³⁺	0.80±0.08	
Cu ²⁺	4.30±0.43	4.40~6.57



Figure 4.1.10 ICP-OES analysis of (a) Cu^{2+} and (b) La^{3+} of the $La(OTf)_3@HKUST-1$ MOF thin films.

Table 4.1.3 Element composition determined by ICP-OES analysis for $La(OTf)_3$ @HKUST-1 MOF thin films.

Name	Wavelength nm	Amount mg/L	Cu/La ratio
La ³⁺	224.700	3.28	
	327.393	3.32	
Cu ²⁺	379.478	0.45	_
	384.902	0.45	7.3

4.1.3.6 Force-field calculations

In order to obtain more detailed information regarding the positions of the molecules within the MOF pores we have carried out force-field based Monte Carlo simulations for different numbers of La(OTf)₃ embedded in HKUST-1, as described in more detail in section 3.4. First, simulations of up to four La(OTf)₃ molecules within a single HKUST-1 unit cell were performed and the binding energies were calculated. To confine the La(OTf)₃ molecules to the cavity an additional harmonic penalty potential (confining potential) was introduced for particles outside the cavity. Results for binding energies and the confining harmonic potential of the lowest energy state are shown in table 4.1.4.

The binding energy is decreasing with an increase of the number of molecules for up to four molecules, as repulsive interactions between the molecules compete with attractive interactions to the MOFs. We note that the confining potential at the energy minimum is increased significantly when more than 3 $La(OTf)_3$ are loaded in each per pore of HKUST-1, which indicates that no more than 3 molecules can fit one pore. A substantial binding energy associated with the loading, which mainly results from the dispersive interaction of the La^{3+} ion, is moved close to the center phenyl ring of one of the BTC ligands at the energy minimum (Fig. 4.1.11).

Table 4.1.4 Binding energies and confining potential for numbers (1, 2, 3, 4) of $La(OTf)_3$ molecular in a single MOF cavity.

HKUST-1 of La(OTf) ₃	binding energy / kcal / mol	confining potential
1	-837.33	6.53
2	-1235.38	49.08
3	-1482.21	47.34
4	-1559.74	152.89



Figure 4.1.11 Schematic structure of single $La(OTf)_3$ (1), 2 $La(OTf)_3$ in (2), 3 $La(OTf)_3$ (3) and in 4 $La(OTf)_3$ HKUST-1 MOF.

Because this interaction may not be fully represented in the force field, we have performed additional DFT calculations to obtain the binding between La^{3+} and the phenyl rings. The calculated binding energy of -7.84 eV is approximately 300 times

kBT at room temperature. In order to compare with the experimental data both cavities were loaded with different numbers of $La(OTf)_3$ and simulation with 10 SA-cycles with 100000 MC steps each, starting at T=750K and cooling down to T=300K, were carried out. The optimized structure with possible locations and number (1, 2, 3, 4) of La(OTf)_3 in the large and middle cavities of HKUST-1 MOF is presented in Fig. 4.1.12a. The simulated out-of-plane XRD data for a (001) growth direction for the optimized structures obtained from the calculations are shown in Fig. 4.1.12b.

The increase of the (004) peak relative to the (002) peak in the calculated XRD data when adding the first La^{3+} close to the Cu^{2+} can be rationalized by considering the fact that this structure can (to first approximation) be described as an *F* lattice, and the intensity of the (002) peaks has to increase because placing the La^{3+} ion close to the Cu^{2+} ions effectively increases the electron density around these Cu positions. When additional La^{3+} ions are placed more close to the middle of the major pore (as in the structures for the 2 and 3 ions by the structure optimizations) the *F*-lattice is effectively changed into an I-lattice (Fig. 4.1.12).

The extinction rules for *I*-lattices lead to a decrease of the (002) peak intensity, as it is evident in the figure for the case of 2 and 3 La^{3+} ions. Further increase of the La^{3+} content in the unit cell leads to an increase of the intensity. This can be explained by the higher atomic scattering factor of the La^{3+} and its position. The former Cu^{2+} *F*-lattice transforms into a La^{3+} *F*-lattice (or even *P*-lattice) with some admixtures of Cu^{2+} in the *I*-lattice positions. The atomic scattering factor for Cu^{2+} cannot fully compensate the La^{3+} contributions to the scattered intensity. The effect explaining the intensity decrease for the 1 La^{3+} and 2 La^{3+} loading state applies also for the higher loading states for La^{3+} . Therefore, an initial Cu dominated structure is not transformed into a La dominated structure. The results fit very well with the experiment data which for the two and three ions are very similar in the out-of-plane data.

By comparing with the results of structure optimizations, loading with a single La^{3+} can be ruled out because for the poor agreement of the simulated with the experimental XRD data. On the other hand a loading with 3 ions per HKSUT-1 unit cell can be ruled out because of the poor agreement with the ICP-OES data. We thus conclude that in the loaded structure 2 La^{3+} ions are hosted within the pore of HKUST-1. This finding is fully consistent with all available experimental and theoretical information.



Figure 4.1.12 (a) Schematic structure of HKUST-1 (1) and after loading different number [single $La(OTf)_3$ (2), 2 $La(OTf)_3$ (3), 3 $La(OTf)_3$ (4) and 4 $La(OTf)_3$ (5)] of $La(OTf)_3$ in HKUST-1. (b) Calculated X-ray diffraction patterns for HKUST-1 before and after loading $La(OTf)_3$ molecular in out-of-plane [empty HKUST-1 (black), single $La(OTf)_3$ (red), 2 $La(OTf)_3$ (blue), 3 $La(OTf)_3$ (magenta) and 4 $La(OTf)_3$ (dark yellow)].

4.1.4 Conclusions

In summary, La(OTf)₃ was successfully loaded into HKUST-1 SURMOF via the solution impregnation method as evidenced by XRD, XPS and ICP-OES data. According to the XRD data, we find that the relative peak intensity of (002) and (004) has a significantly decrease after loading La(OTf)₃. In addition, the XPS and ICP-OES results reveal that two La³⁺ ions have been loaded into one pore of HKUST-1. These data are fit very well with the simulation results preformed by using a refined force-field analysis. The pristine HKUST-1 structure is described as an F lattice. After loading La(OTf)₃, the La³⁺ ions are placed more close to the middle of the major pore and change the F-lattice into I-lattice. This structure is stabilized by pronounced dispersive interactions between the La³⁺ and the phenyl ring of a BTC ligand. The resultant loading of La (and other noble metal) species into porous solids is of pronounced interest with regard to using MOF thin films for applications. In future work we plan to study the electrochemical properties of the loaded SURMOFs which also offer rich potential for catalysis applications.

4.2 Bi₂O₃ nanoparticles encapsulated into HKUST-1 SURMOF

As discussed above in section 4.1, the metal ions were successfully loaded into MOFs by impregnation method using the phenyl ligands as nucleation centers. In this section, we extend the study from metal@SURMOF to oxide@SURMOF systms and prepare quantum-sized Bi₂O₃ NPs in HKUST-1 SURMOF by the same methodology as La ions loading.

4.2.1 Background

Photocatalysts carry a huge potential for the removal of contaminations from the environment and have been demonstrated to show an impressive performance in decomposing organic pollutants under UV-light irradiation.^[127] Among the numerous semiconducting materials under investigations, recently much attention has been given to Bi_2O_3 photocatalysts. Bi_2O_3 exhibits narrow electronic band gaps (2.8eV or less) and shows *p*-type behavior with a high photocatalytic activity.^[128] Straightforward applications, however, are hampered by the fact that the fabrication of monodisperse Bi_2O_3 nanoparticles (NPs) with well-defined diameters represents a major challenge. Conventional NP synthesis methods typically yield rather broad NP size distributions.^[3] For the fabrication of high performance photocatalysts as well as for a more detailed understanding of the fundamental photocatalytic process, the development of novel synthesis allowing to produce Bi_2O_3 clusters and NPs with narrow size distributions and large surface areas is urgently required.

A very appealing strategy to reach this goal is the synthesis of NPs inside the voids of metal–organic frameworks (MOFs).^[13, 14] Since the pore-walls of the MOF can be used to control the size of the NPs; as a result of its pore sizes and large loading capacity for guest species, this class of highly porous, crystalline materials provides an ideal platform for the encapsulation of catalytically active compounds (such as Pt,^[78] Au,^[79] Ti-based^[80]) as well as of photosensitizers.^[129] The formation of large Pd-clusters after libration of Pd from [(tmeda)Pd(CH₃)₂] (tmeda=N,N,N',N' tetramethyl-ethylenediamine) has been reported by Fischer et al.^[130] MOFs are typically insulators, the size of the band-gap strongly depends on the nature of the organic ligands used to build the molecular frameworks. During the past decade, an increasing number of work has been reported using MOFs as a host matrix, which after loading with appropriate compounds act as a high-yield photocatalyst with a number of interesting properties, e.g. for hydrogen evolution (Pt@MOF)^[78] and light-driven α -alkylation reactions (BCIP@MOF).^[131]



Figure 4.2.1 Synthesis scheme of Bi₂O₃@HKUST-1 SURMOFs.

Here, we use the pores within the HKUST-1 SURMOFs for the synthesis of Bi_2O_3 clusters/NPs, yielding a novel Bi_2O_3 @HKUST-1 (or $Cu_3(BTC)_2$, BTC = 1,3,5-benzene-tricarboxylic acid) hybrid-photocatalyst. The layer-by-layer strategy was used to fabricate this SURMOF material, since they are crystalline, oriented and exhibit a well-defined thickness and can be manufactured with thickness in the micrometer-range. The final hybrid-photocatalysts formed by this novel synthesis procedure consists of *p*-type Bi_2O_3 NPs embedded into the HKUST-1 SURMOF (Fig. 4.2.1).

When the crystallite dimension of a semiconductor particle falls below a critical radius of approximately 10 nm, the charge carriers behave quantum mechanically, the band gap increases and the band edges shift to yield larger redox potentials. Thus, the use of quantum-sized Bi_2O_3 semiconductor NPs (1-3 nm) may result in increased photo-efficiencies for the systems in which the rate-limiting step is the charge transfer.

4.2.2 Preparation of the Bi₂O₃@HKUST-1 SURMOF

All HKUST-1 SURMOFs used in the present work were grown on modified Au substrates using spray method, except parts of TEM and UV-Vis samples were grown on quartz glass, as described in more detail in section 1.3.2.1. Before further processing, all SURMOFs samples were activated by ultrasound in dichloromethane solution for 5 min to remove residual solvent from the SURMOFs pores and characterized by XRD.

For BiPh₃ loading, a HKUST-1 SURMOF was placed into a 250 ml flask, which was then evacuated to 200 Pa at room temperature for 30 min. Subsequently, a freshly prepared solution of BiPh₃ in ethanol (1 mM, Aldrich) was injected quickly into the reaction flask and heated to 65 °C for 36 h.

After loading BiPh₃, the reaction flask with BiPh₃@HKUST-1 sample was taken out from the oven and irradiated with 255 nm UV light for 5 h. Subsequently, the sample was removed from the reaction solution, rinsed with pure ethanol and dried in dry N₂ gas. Then, the sample was irradiated with 255 nm UV light for 1 h. After loading all samples were characterized by XRD before further measurement.

4.2.3 Photolysis of the Bi(Ph)₃ precursor

BiPh₃ is a simple organo-bismuth compound which is quite stable under normal conditions. According to previous reports, the photo-decomposition of BiPh₃ in solution in the presence of O₂ leads to the formation of Bi₂O₃ particles.^[132] Upon irradiation, the color of the solution turns from clear to opaque (Fig. 4.2.2). This observation reasonably supports above that Bi(Ph)₃ has been breaking down gradually into large size Bi₂O₃ NPs in the solution. Dynamic light scattering (DLS) demonstrates a particle size distributions from 120 nm to 1 μ m (Fig. 4.2.3).



Figure 4.2.2 BiPh₃ ethanolic solution before irradiation (left) and after irradiation (right).



Figure 4.2.3 Dynamic light scattering (DLS) analysis for BiPh₃ ethanolic solution after irradiation.

Qualitative analyses of the XPS (Fig. 4.2.4) proves that the photolysis products show a characteristic Bi $4f_{5/2}$ peak with a binding energy shift from 167.1 eV to 164.8 eV, which describes the successful UV-decomposition of the BiPh₃ precursors into Bi₂O₃ NPs. The calculated atomic ratio of Bi/O amounts to 2:3, which also demonstrated that the photolysis product is Bi₂O₃.^[133]



Figure 4.2.4 XPS analysis for BiPh₃ (up) and Bi₂O₃ (down).

The UV-Vis analysis also proves the degradation product is Bi_2O_3 (Fig. 4.2.5). In the previous report, Bi_2O_3 has several crystal structures including α -, β -, and γ - phases, with an indirect band gap of 2.6 to 2.9 eV, which differs for different crystal structures. Here, we calculated the band-gap E_g of the degradation product using the following empirical formula:

$$E_g = \frac{1240}{\lambda} = \frac{1240}{459} \approx 2.7eV \tag{1}$$

Since the band gap of this semiconducting material is 2.7 eV which agrees with the band gap of Bi_2O_3 reported previously. This demonstrates the existence of α - phase Bi_2O_3 NPs.



Figure 4.2.5 UV-Vis analysis of the Bi_2O_3 thin films on quartz glass (black) and the band gap versus wavelength of the Bi_2O_3 thin films is approximated using the direct band gap method by plotting the absorbance squared versus energy, and extrapolating to zero (dotted line).

4.2.4 Results and discussion

4.2.4.1 Quantitative analysis of BiPh₃ loading into the HKUST-1 SURMOF by QCM

The loading of $BiPh_3$ into the HKUST-1 SURMOFs was analyzed in a quantitative fashion using a QCM (Fig. 4.2.6). The HKUST-1 SURMOFs used here were grown on modified Au QCM sensor, as described in more detail in section 1.3.2.4.

The mass density of the activated framework amounts to 0.98 g·cm⁻³, which is increased by the ethanol contained in the pores, yielding a total mass-density of the ethanol-soaked HKUST-1 of 1.53 g·cm⁻³. A quantitative analysis of the QCM yields a BiPh₃ loading of ~0.17 g BiPh₃ per 1 g ethanol-soaked HKUST-1. This corresponds to a loading of 2 to 3 BiPh₃ molecules per HKUST-1 unit cell.



Figure 4.2.6 Layer-by-layer growth of the HKUST-1 SURMOF on the QCM sensor with 20 cycles and performed uptake experiment with BiPh₃. The inset is a magnification of the layer-by-layer growth of the SURMOF. (The small oscillations in the curve are from the pump).

4.2.4.2 XRD analysis of the Bi₂O₃@HKUST-1 SURMOF

According to the XRD data (Fig. 4.2.7), we present an out-of-plane geometry for the pristine, monolithic and oriented HKUST-1 SURMOFs thin film (Fig. 4.2.7 black). As reported in previous works,^[74] the (002) and (004) peaks are sharp and well-defined. Their relative intensities are in full agreement with simulations assuming perfect HKUST-1 material (Fig. 4.2.7b black). The absence of diffraction peaks for other crystallographic directions in the out-of-plane data reveals that the SURMOFs growth proceeds only along the (001) crystallographic direction.

The XRD data recorded after immersion of the HKUST-1 thin film into the BiPh₃ solution (Fig. 4.2.7b, red) reveal that loading the guest molecules does not affect the crystallinity of the host matrix. Although no new diffraction peaks appear, after loading the ratio of the diffraction peak intensities is different. The (002)/(004) (out-of-plane data) ratio has decreased from 2.13 for the pristine film to 0.79 for the BiPh₃ loaded film. Longer immersion times did not lead to a further change of the relative XRD peak intensities. This change in form factor confirms that host molecules are loaded because such thin coating would not lead to a change of the relative XRD peak intensities form factors.



Figure 4.2.7 X-ray diffraction patterns recorded: (a) calculated XRD pattern for HKUST-1 [empty HKUST-1 (black) and after loading 3 BiPh₃ (red)] and (b) experimental XRD data recorded in out-of-plane [empty HKUST-1 (black), after loading BiPh3 (red), and after UV light irradiation (blue) scattering geometry].

In order to obtain more detailed information regarding the positions of the molecules within the MOF pores we have carried out force-field based Monte Carlo simulations for different numbers of BiPh₃ embedded in HKUST-1, as described in the section 3.3.

HKUST-1 contains three types of cavity: large, middle and small cages (Fig. 4.2.8). The small cavity is typically not considered because the pore-diameter is much smaller than the other pores (less than 0.9 nm). The optimized structure with possible locations and numbers (1, 2 and 3) of BiPh₃ in HKUST-1 MOF is presented in Fig. 4.2.8. The simulated XRD data of the (001), (010) and (100) crystallographic direction in different loading numbers are also presented here.

We further suggest a model where 3 BiPh₃ are uniformly loaded within the HKUST-1 pores. Force-field based simulations have been carried out to obtain the precise position of BiPh₃ molecules in the HKUST-1 lattice, as reported previously for other molecular guests in HKUST-1.^[134] The best agreement of XRD-data simulated for the different structures with the experimental XRD is obtained for 3 BiPh₃ molecules per HKUST-1 unit cell (Fig. 4.2.7 red and Fig. 4.2.8 (8) black) which is also consistent with the QCM-data.



Figure 4.2.8 Schematic structure of HKUST-1 (1) (large pore: A red, middle pore: B yellow and small pore: C green) and after loading different number [single Bi^{3+} in A (1), single Bi^{3+} in B (2), 2 Bi^{3+} in A (3), 1 $Bi(Ph)_3$ in A and 1 Bi^{3+} in B (4), 2 Bi^{3+} in B (5), 3 Bi^{3+} in A (6), 2 Bi^{3+} in A and 1 Bi^{3+} in B (7), 1 Bi^{3+} in A and 2 Bi^{3+} in B (8), 3 Bi^{3+} in B (9)]. Calculated X-ray diffraction patterns for HKUST-1 before and after loading Bi^{3+} in different plane [(001) plane (up, black line), (010) plane (middle, red line) and (100) plane (down, green line)]. The anion was hidden.

We now turn our attention to the UV-induced nanoparticle synthesis inside the MOF pores. XRD data (Fig. 4.2.7b) reveal that the crystallinity of the MOF host lattice is not affected by the reaction. After the photoreduction, the XRD-data reveal a small shift to smaller diffraction angles, indicating a very slight (0.24 %) expansion of the HKUST-1 unit cell. The (002)/(004) intensity ratio only shows a fairly small change, a slight increase from 0.79 to 1.05 (Fig. 4.2.7b, blue). Since the intensity ratio is clearly different than that seen for the empty HKUST-1, a pronounced sintering with the formation of large clusters embedded in the metal-organic framework can be excluded.

4.2.4.3 TEM and SEM analysis of the Bi₂O₃@HKUST-1 SURMOF

In order to further characterize the NP@MOF hybrid material, we have carried out investigations using TEM. In this context it should be noted that SURMOFs are particularly well suited for TEM investigations since they can be detached from the substrate, yielding flakes with well-defined thickness and orientation. The HAADF-STEM data shown in Fig. 4.2.9a reveal the presence of Bi₂O₃ NPs with sizes of 1-3 nm distributed very uniformly within the HKUST-1. SAED (small area electron diffraction) data (Fig. 4.2.9b) show a well-defined diffraction pattern which is fully consistent with the (111) orientation XRD diffraction data (SURMOF was grown on quartz glass facing a (111) orientation). HR-TEM diffraction pattern are further discussed in the Tab. 4.2.1.

SAED	HKUST-1 (111)			
d / nm	d / nm			
		Н	К	L
0.915	0.930	2	2	0
0.547	0.537	2	2	4
0.470	0.465	4	4	0
0.359	0.351	2	4	6
0.310	0.310	6	6	0
0.265	0.268	4	4	8
0.222	0.213	6	4	10

Table 4.2.1 SAED (Selected Area Electron Diffraction) data and lattice spacing (d) for comparison between electron diffraction and XRD data of [111] oriented HKUST-1.



Figure 4.2.9 (a) HAADF-STEM images of $Bi_2O_3@HKUST-1$ SURMOFs. (b) SAED (Selected Area Electron Diffraction) patterns the $Bi_2O_3@HKUST-1$ SURMOFs. (c) Example EDX analysis of $Bi_2O_3@HKUST-1$ SURMOFs.

After photoreduction in the presence of O_2 we propose that $(Bi_2O_3)_n$ clusters are formed. Since the TEM images show a sharp, but not completely uniform size distribution we conclude that during the photoinduced cluster formation Bi-containing species can diffuse in neighboring pores to form larger clusters. Previous theoretical work has shown that various stoichiometric and neutral, closed-shell $(Bi_2O_3)_n$ clusters with n = 1-5 clusters are stable.^[135] Such $(Bi_2O_3)_n$ NPs of different sizes are schematically depicted in Fig 4.2.10.



Figure 4.2.10 Schematic structure of (a) empty HKUST-1; (b) Infiltration of three $BiPh_3$ molecules inside an HKUST-1 pore; (c) Model of photosynthesized preliminary Bi_2O_3 Clusters/NPs; (d) Model of photosynthesized $(Bi_2O_3)_n$ Clusters/NPs with n = 1-5 in the defined pore-space of HKUST-1, avoiding sintering with particles from adjacent pores.

The morphologies of HKUST-1 thin film were characterized by SEM (Fig. 4.2.11). Cross-sectional images recorded by SEM demonstrate that the thickness of SURMOFs amounts to about 100 nm (Fig. 4.2.11 down). The SEM pictures show that a continuous, compact and homogeneous SURMOF was successfully prepared. After the encapsulation of Bi_2O_3 nanoparticles inside HKUST-1 SURMOF, the morphology does not show significant changes. In addition, we did not observe a large amount of Bi_2O_3 NPs deposited on the surface of HKUST SURMOF.



Figure 4.2.11 Scanning electron micrograph (SEM) of 20 cycles of HKUST-1 MOF thin films (left) and after loading Bi_2O_3 (right).

4.2.4.4 ToF-SIMS analysis of Bi₂O₃ NPs in HKUST-1 SURMOF

The presence of small $(Bi_2O_3)_n$ NPs is also demonstrated by ToF-SIMS carried out for the loaded HKUST-1 thin film, where the cluster of the BiO^+ , $Bi_2O_2^+$, $Bi_3O_4^+$ and Bi_2O^+ were detected (Fig. 4.2.12, 4.2.13 and 4.2.14).

As shown in Figs. 4.2.12 and 4.2.13, the positive polarity secondary ion mass spectrum obtained under quasi-static conditions from a $Bi_2O_3@HKUST-1$ SURMOF stack is dominated by several bismuth oxides and $Bi_xO_yCu_z$ cluster ions. The bismuth oxide fragment Bi_2O shows highest intensity (212 kcts) followed by Bi_3O_4 (170 kcts), Bi_4O_5 17 (kcts), and Bi_5O_7 (39 kcts). A marked drop in intensity is observed for bismuth oxide clusters bigger than Bi_5O_9 . Bi_6O_9 is not detectable, Bi_7O_{10} has an intensity of only 1 kcts. In addition, sputtering with a high current oxygen beam under dynamic SIMS conditions leads to the appearance of gold peaks originating from the Au substrate on which the $Bi_2O_3@HKUST-1$ SURMOF was deposited. The new cluster ions like $CuAu_2$ are formed due to the mixing process during ion bombardment.

Stable and closed shell cationic bismuth oxide clusters with the general formula $(Bi_2O_3)_nBiO^+$ (1<n<4) have been reported in previous studies.^[136] Although some exchange of small species (particles with diameters smaller than the channel width in HKUST-1 MOFs of about 1.2nm) between adjacent pores within the MOF is possible, a sintering of larger particles formed in the reaction can be ruled out. According to the TEM-data, $(Bi_2O_3)_n$ –NPs have sizes between 1 to 3 nm (Figure 4.2.10). Our results thus demonstrate that pores within MOFs offer a unique opportunity for the synthesis of NPs with small size distributions.



Figure 4.2.12 Quasi-static SIMS of a Bi_2O_3 @HKUST-1 SURMOF stack performed with C_{60} (20 keV) bunched. 400 < m/z < 750.



Figure 4.2.13 Quasi-static SIMS of a Bi_2O_3 @HKUST-1 SURMOF stack performed with C_{60} (20 keV) bunched. 950 < m/z < 1700



Figure 4.2.14 Dynamic SIMS of a $Bi_2O_3@HKUST-1$ SURMOF stack performed with C_{60} (20 keV, 0.1 pA) bunched analysis beam and O_2 (500 eV, 110 nA) sputter beam. 400 <

m/z < 700.

4.2.4.5 Mott–Schottky analysis of HKUST-1 SURMOFs obtained before and after Bi₂O₃ encapsulation

In order to determine charge separation processes at the $Bi_2O_3@HKUST-1$ oxide-organic interface, Mott–Schottky measurements have been performed in 0.5 M Na_2SO_4 water/EtOH (1:3) solution, which was connected in three-electrode mode, consisting of an Ag/AgCl reference electrode with a Pt counter electrode (Fig. 4.2.15).



Figure 4.2.15 Schematic of the electrochemical cell with the three electrodes set-up. Electrolyte 0.5 M NaSO₄ Water/EtOH (1:3) solution, electrode area 0.5 cm².

As shown in Fig. 4.2.16a, the negative slope indicates a *p*-type behavior of Bi₂O₃. Characteristic Mott–Schottky measurement provides a flat-band potential of pure Bi₂O₃ at around 0.64 V *vs. RHE*. In contrast to the Bi₂O₃, HKUST-1 indicates an *n*-type behavior with a potential of 1.27 V *vs. RHE* (Fig. 4.2.16b). Nevertheless, it is difficult to acquire standard *n*-type curve of the HKUST-1 due to different intrinsic impurities. Moreover, the Mott-Schottky curve of the Bi₂O₃@HKUST-1 SURMOF reveals a *p*-*n* junction behavior (Fig. 4.2.16c). Accordingly to these measurements, we propose in Fig. 4.2.16d a possible mechanism for the efficient charge separation at the *p*-*n* junction interface of Bi₂O₃@HKUST-1. The *p*-type Bi₂O₃ NPs embedded into an *n*-type HKUST-1 are brought into close contact forming an efficient *p*-*n* junction, the photoinduced holes in the *n*-type HKUST-1 move to the higher potential *p*-type Bi₂O₃ NPs, while the photoinduced electrons in the *p*-type Bi₂O₃ NPs move to the lower potential of the *n*-type HKUST-1. The internal electric field formed at the concrete *p*-*n* oxide-organic interface can be efficiently separated though its highly porous and monolithic SURMOF array structure.



Figure 4.2.16 Capacitance data plotted in Mott-Schottky representation for (a) Bi_2O_3 , (b) HKUST-1 and (c) Bi_2O_3 @ HKUST-1. Electrolyte 0.5 M NaSO₄ Water/EtOH (1:3) solution, electrode area 0.5 cm². (d) Band gap relationship between n-type Bi_2O_3 and p-type HKUST-1.

4.2.4.6 Photocatalytic activity of Bi₂O₃@HKUST-1 SURMOF

The photocatalytic activity of $Bi_2O_3@HKUST-1$ was demonstrated using a standard test reaction, the degradation of a common dye, NFR. In order to determine the catalyst activity, we prepared a solution of NFR and then immersed the Bi_2O_3 NP-loaded SURMOFs into the corresponding container. Dynamic UV-Vis apparatus used in this experiment was shown in Fig. 4.2.17



Figure 4.2.17.Schematic drawing of the dynamic photo-decomposition apparatus for the photocatalytic activity measurement.

The concentration of the NFR dye was determined by measuring the absorbance at $\lambda_{max} = 557 \text{ nm}$ (Fig. 4.2.19c). As shown in Fig. 4.2.19b, five cases, pristine solution [40 μ M water/EtOH (1:3) NFR solution], Bi₂O₃@HKUST-1 (~ 7 μ g/cm², 4 cm², mass ~ 28 μ g), HKUST-1 (~ 6 μ g/cm², 4 cm², mass ~ 24 μ g), Bi₂O₃ (mass ~ 30 μ g) and Au wafer (4 cm²), immersed in 30 mL solution of the dye (40 μ M) were studied. The decrease of the absorption conveniently allows to study the adsorption of the NFR dye on the surface of the powder Bi₂O₃ particles and their diffusion into the empty and the Bi₂O₃ NP loaded SURMOFs. This information is highly relevant since the Bi₂O₃ NPs encapsulated in the MOF are expected to be photocatalytically active for NFR decomposition, and the NFR molecules should to be able to diffuse inside the MOF lattice.

The corresponding adsorption determined from the reduction of the absorption in the liquid is shown in Fig. 4.2.19a (also shown in Fig. 4.2.18) and amounts to 3.2% (NFR dye mass ratio in solution) for the empty MOF and 2.6% for the NP loaded SURMOF. The adsorption on the powder material only to amounts 0.7%. A quantitative analysis of the decrease of 3% yields a loading of ca. 1-2 NFR dye molecules per MOF pore.



Figure 4.2.18 UV-Vis absorption spectra of HKUST-1 SURMOFs (black), $Bi_2O_3@HKUST-1$ SURMOFs (red) and $Bi_2O_3@HKUST-1$ SURMOFs after absorption of NFR dye 1 h (blue).

After loading of Bi₂O₃ NPs the adsorption is only slightly decreased, indicating that the diffusivity of the NFR molecules inside the MOF is essentially unaffected by the loaded Bi₂O₃ NPs. After about one hour the concentration of the NFR molecules in the solution has reached a stable value and no further reduction of the absorption was observed, demonstrating that no decomposition of the NFR dye took place in the dark. When UV-light (255nm) was turned on, a gradual reduction of NFR-concentration was observed, directly demonstrating the photocatalytic decomposition of the NFR dye molecules. The corresponding concentrations as a function of time are presented in Fig. 4.2.19b. In the next step, the solutions were exposed to 255 nm UV light. 100% degradation of NFR was achieved in the presence of Bi₂O₃@HKUST-1 thin film within 5 hours. This result clearly indicates that the Bi₂O₃@HKUST-1 thin film is the most efficient sample for the photodegradation of NFR dye. Reference experiments for the pure HKUST-1 and (non-encapsulated) Bi₂O₃ yielded a degradation of 44% and 74% degradation of NFR under same conditions, respectively. These results demonstrate that the NPs@MOFs system exhibits a significant photochemical activity for the degradation of NFR dye which is larger than that of the individual components. The regeneration and reusability of Bi₂O₃@HKUST-1 was investigated by repeating at least four times the NFR degradation. The photocatalyst was immersed in fresh NFR solutions and exposed to UV irradiation for 1 h. As shown in Fig. 4.2.19d, no deactivation of the photocatalyst is observed after four consecutive runs.



Figure 4.2.19 (a) The absorption of NFR dye in the HKUST-1 SURMOF (black), Bi₂O₃@HKUST-1 SURMOF (red) and powder Bi₂O₃ (blue). (b) Photodegradation with different catalytic conditions [empty (black), Bi₂O₃@HKUST-1 SURMOF (red), HKUST-1 SURMOF (blue), powder Bi₂O₃ (dark yellow) and gold wafer (magenta)] under UV light irradiation. (c) UV-Vis absorption spectra of the NFR dye irradiate different time with the Bi₂O₃@HKUST-1 photocatalyst. (d) Four repeated processes of using the Bi₂O₃@HKUST-1 photocatalyst for photodegradation of NFR under UV light irradiation.

4.2.4.7 Stability of the Bi₂O₃@HKSUT-1 SURMOF by XRD

The stability of the Bi₂O₃@HKSUT-1 SURMOF in NFR dye solution was measured upon immersing the sample in dye solution for 5h, 10h, 15h and 20h (Fig. 4.2.20). No significant change was observed in the XRD pattern suggesting the SURMOF is stable in dye solution. In addition, after five cycles of repeated use for photocatalytic dye solutions, no decomposition or structural changes in the Bi₂O₃@HKSUT-1 SURMOF were detected (Fig. 4.2.21). These findings demonstrate that new photacatalyst can be recycled and used several times.



Figure 4.2.20 XRD patterns for Bi_2O_3 @HKUST-1 SURMOF in NFR@EtOH/H₂O solution for different times.



Figure 4.2.21 XRD patterns for Bi₂O₃@HKUST-1 SURMOF before and after reaction.

4.2.4.8 Degraded solution analysis by ESI-MS

In addition, we have carried out measurements using ESI-MS for the solution after UV-exposure (Fig. 4.2.22b). The color of test solutions is show in Fig. 4.2.23. The results allow for identifying six intermediate species (Fig. 4.2.22a) occurring in the course of NFR photo degradation. Based on the intermediates identified, a possible degradation pathway of the NFR dye is proposed, for details see Fig. 4.2.22a. As shown in Fig. 4.2.22, the application of the Bi₂O₃@HKUST-1 SURMOF catalysis system leads to an efficient photodegradation of the parent compound, NFR, and to an enhanced formation of smaller photodegradation products.



Figure 4.2.22 (a) Proposed degradation pathway of NFR using the Bi_2O_3 @ HKUST-1 SURMOF for the photodegradation of NFR under UV light irradiation. (b) ESI-MS of the NFR solution (top), NFR solution after UV light exposure with Bi_2O_3 @HKUST-1 SURMOF (middle), and NFR solution after UV light exposure without any catalyst (bottom).



Figure 4.2.23 The pristine (a), after photo-degradation with Bi₂O₃@ HKUST-1

SURMOF (b) and after UV-light irradiation (c) of the NFR dye solution under sun light (left) and UV-light (right) environment.

4.2.5 Conclusions

We report on a novel synthesis strategy to fabricate an efficient and recyclable, hybrid-photocatalyst. Such Bi₂O₃@HKUST-1 system hybrid-photocatalyst is prepared by photodecomposition of BiPh₃ loaded into the pores of a metal-organic framework, yielding Bi₂O₃-particles of rather uniform size distribution encapsulated into the pores of the MOF. This quantum-sized Bi₂O₃ semiconductor NPs (1-3 nm) in the HKUST-1 are expected to show increased photo-efficiencies for the reactions in which the rate-limiting step is the charge transfer. The hybrid Bi₂O₃@HKUST-1 SURMOFs photocatalyst can be easily separated and recycled and shows no significant loss in the photocatalytic activity.

In comparison to the powder Bi_2O_3 photocatalysts used in the photocatalytic degradation of dye, such Bi_2O_3 @HKUST-1 thin film photocatalysts are efficient, green, cheap and more suitable for upcoming clean technology applications. Further investigations are currently underway in our laboratory to prepare novel SURMOF based photocatalytic membranes in a flow-through fashion for the UV-induced degradation of organic pollutants from wastewater.

5 Loading metal ions into SURMOFs by using side chain of ligands as nucleation centers

To increase the number of available nucleation centers in MOFs, adding side-chains with functional groups to the organic linker is an effective method. The side-chain with functional groups can largely enhance the uptake capacity of metal ions while the crystal structure remains unchanged. However, there is large difficulty in theoretical analysis and experimental study due to the introduction of side-chains.

5.1 Loading of metal ions into functionalized SURMOF with sulfur and alkene side-chains

5.1.1 Background

The porous structure of MOFs^[13, 14] resulting from their flexible pore sizes and large loading capacity for guest molecules, making them an ideal platform to some well-known applications (such as biomedicine,^[137] chemical sensors,^[7] separations^[138] and catalysts^[15]). During the past decade, an interesting investigation of MOF materials is to assemble with different functional groups to their organic ligands, such as amino,^[139] azide,^[140] and thiol.^[141] By doping with different amounts and types of side-chains, the performance of MOF material can be significantly improved, which paves the way for their application in different fields, e.g., drug delivery,^[70] sensors^[67] and gas adsorption.^[142]

A very appealing application of this functionalized MOF is the loading of guest species, in particular metal and metal ions.^[143] Usually, directly growing of metal ions into a MOF lattice is difficult because of the low nucleation centers in the MOF.^[81] Therefore, the nucleation centers, which are directly related to the adsorption capacity of metal ions uptake, will substantially increase by adding some functional groups into the ligands of MOF. He and co-workers have reported a novel sulfur-MOF-5 with addition of sulfur-conjugated functional groups on the BDC linker.^[25] This functionalized side-chain tends to bind with the noble-metal species and to trigger a color change.

In this section, we used LPE techniques to fabricate the $Cu_2(atBDC)_2(dabco)$ SURMOF, (Fig. 5.1a and b) on a QCM sensor which allows to monitor an accurate mass change during growth and loading process. QCM was demonstrated to be a simple but efficient way to investigate the uptake behavior of SURMOF in a previous study.^[144] We have obtained the total mass uptake of the $Cu_2(atBDC)_2(dabco)$ SURMOF for a series of metal ions, and the largest adsorption capacity was determined for Fe³⁺ and

 Pd^{2+} uptake. In addition, we demonstrate that the sulfur and alkene side-chain in the ligand will improve the adsorption capacity of MOFs for Fe³⁺ and Pd²⁺ uptake, but at the same time they will block the metal ions diffusion by comparing the diffusivities of Cu₂(atBDC)₂(dabco) with Cu₂(BDC)₂(dabco) SURMOF.



Figure 5.1 (a) Schematic illustration of $Cu_2(atBDC)_2(dabco)$ SURMOF. (b) The structure formula of atBDC molecule.

5.1.2 Preparation of the Cu₂(atBDC)₂(dabco) SURMOF

All SURMOF samples used in this work were grown on modified Au surface, except UV-Vis samples were grown on quartz glass. The surface modification was carried out by depositing a SAM made from MUD for the Au substrates, as described in more detail in section 3.2. The surface treatment of quartz glass was carried out by O₂ plasma cleaning, as described in more detail in section 3.3.

The SURMOFs samples used to uptake analysis were fabricated by a QCM system, as described in more detail in section 1.3.2.4. Gradually adding metal solution and ligand solution leads to a stepwise increase of the deposited layers in mass which corresponds to the layer-by-layer growth of SURMOF on the sensor surface (Fig. 5.2). This method can be directly used for further experiments such as monitoring of adsorption/desorption of guest molecules into SURMOFs.^[107] The pumping times were 10 min for the copper acetate solution and 20 min for the atBDC solution. Each step was followed by a rinsing step (5min) with pure ethanol to remove residual reactants. A total of 25 growth cycles were used for all SURMOFs investigated in this work.

Other samples for XRD, IR and UV-Vis characterization were fabricated by a pump system

with the same parameters of QCM system (reaction temperature, solution concentration, numbers of growth cycles and reaction time), as described in more detail in section 1.3.2.2. Before further processing, all SURMOF samples were characterized by XRD (Fig. 5.3 and Fig. 5.4).



Figure 5.2 Layer-by-layer growth of the $Cu_2(BDC)_2(dabco)$ (lift) and $Cu_2(atBDC)_2(dabco)$ (right) SURMOF on the QCM sensor with 25 cycles. The inset is a magnification of the layer-by-layer growth of the SURMOF.

5.1.3 Results and discussion

5.1.3.1 XRD analysis of Cu₂(atBDC)₂(dabco) SURMOF

According to the XRD data [Fig. 5.3 (growth on gold substrate) and Fig. 5.4 (growth on QCM sensor)], we present an out-of-plane geometry for the pristine, monolithic and oriented SURMOFs. As reported in previous works,^[75] the (001) peaks on MUD-SAM are well-defined and sharp (Fig. 5.3 left red), their relative intensities are in full agreement with simulations assuming perfect Cu₂(BDC)₂(dabco) SURMOF (Fig. 5.3 left blue). Nevertheless, the intensity of (002) peak is much larger in the simulation than in the experiment. The reason is that the crystal structure of MOF is not understood. The absence of diffraction peaks for other crystallographic directions in the out-of-plane data reveals that the SURMOFs growth proceeds only along the (001) crystallographic directions, which supports this orientation structure (Fig. 5.3 right red). Compared with the Cu₂(BDC)₂(dabco) SURMOF, Cu₂(atBDC)₂(dabco) SURMOF has got the same diffraction angle in the XRD patterns. This demonstrates that the crystal structure of Cu₂(atBDC)₂(dabco) SURMOF is similar to Cu₂(BDC)₂(dabco) SURMOF.



Figure 5.3 X-ray diffraction patterns recorded for $Cu_2(atBDC)_2(dabco)$ (black), $Cu_2(BDC)_2(dabco)$ (red), simulation of (001) orientation (blue) and simulation of powder (magenta) of SURMOFs.



Figure 5.4 X-ray diffraction patterns recorded for $Cu_2(atBDC)_2(dabco)$ (black) and $Cu_2(BDC)_2(dabco)$ (red) of SURMOFs on QCM sensor.

5.1.3.2 IR and UV-Vis analysis of Cu₂(atBDC)₂(dabco) SURMOF

The characterization of $Cu_2(atBDC)_2(dabco)$ SURMOFs was carried out using IR (Fig. 5.5) and UV-Vis spectroscopy (Fig. 5.6). For comparison, the IR spectrum of

 $Cu_2(BDC)_2(dabco)$ SURMOF was also presented. The spectrum shows intense broad band at 1628 cm⁻¹ which are assigned to vibrations of COO⁻ of pristine $Cu_2(BDC)_2(dabco)$ SURMOF (Fig. 5.5 red). The frequencies of these bands agree with the values reported previously for pristine $Cu_2(BDC)_2(dabco)$ SURMOF.^[145] In contrast to the $Cu_2(BDC)_2(dabco)$, a new characteristic vibration at 924 cm⁻¹ (R-CH=CH₂) has appeared in the spectrum of the $Cu_2(atBDC)_2(dabco)$ SURMOF sample (Fig. 5.5 black) which indicates that alkene functional groups exist. The characteristic absorption bands of $Cu_2(atBDC)_2(dabco)$ and $Cu_2(BDC)_2(dabco)$ SURMOF are summarized in table 5.1. The UV-Vis results show an absorption change in the range of 324-424 nm between the $Cu_2(atBDC)_2(dabco)$ SURMOF and $Cu_2(BDC)_2(dabco)$ SURMOF which is attributed to the absorption of thioether bond of the side-chain (Fig. 5.6).



Figure 5.5 IR spectrum for $Cu_2(atBDC)_2(dabco)$ (black) and $Cu_2(BDC)_2(dabco)$ (red) of SURMOFs.

Table 5.1 Band assignment for the IR spectrum of $Cu_2(atBDC)_2(dabco)$ and $Cu_2(BDC)_2(dabco)$ on MHDA SAM.

Cu ₂ (atBDC) ₂ (dabco)	Cu ₂ (BDC) ₂ (dabco)	Absorption band (cm ⁻¹)	Assignment
V	٧	1628	(COO ⁻) asymm. Skretching
V	V	1497, 1427, 1372	(CH ₂) (from dabco)
V		1403, 1266, 1097	(CH ₂) (from –CH ₂ -S-)
V		923	(-C-H) (from -CH=CH ₂)



Figure 5.6 UV-Vis spectrum for $Cu_2(atBDC)_2(dabco)$ (black) and $Cu_2(BDC)_2(dabco)$ (red) of SURMOFs.

5.1.3.3 Quantitative analysis of metal ions loaded into Cu₂(atBDC)₂(dabco) SURMOF by QCM

The quantitative analysis of metal ions adsorption was performed using QCM uptake experiments. As shown in Fig. 5.7, a series of metal nitrate compounds (such as $Zn(NO_3)_2$, $Ag(NO_3)$, $Pd(NO_3)_2$, $Fe(NO_3)_3$, $Cd(NO_3)_2$, $Ni(NO_3)$, $Co(NO_3)_2$) were investigated by using impregnation method. The entire metal compound solutions used in experiments was prepared at same concentrations (0.1 mM) by dissolving the inorganic compounds into ethanol. The maximum uptake capacities for Fe³⁺ and Pd²⁺ are 3.2 µg·cm⁻² and 2.0 µg·cm⁻², respectively. This corresponds to a loading of 6 Fe³⁺ and 4 Pd²⁺ molecules per pore of Cu₂(atBDC)₂(dabco) SURMOF (Fig. 5.7 green and blue). However, the uptake rates of Ag⁺ and Co²⁺ are much lower (Fig. 5.7 red and wine). The uptake capacities of Au⁺ and Co²⁺ are 0.6 molecules per pore (0.45 µg·cm⁻²) and 0.48 molecules per pore (0.25 µg·cm⁻²), respectively. More interestingly, the adsorption capacities of the Zn²⁺, Cd²⁺, Ni⁺ amount nearly to zero which means that there is little obvious physical adsorption of these cations in Cu₂(atBDC)₂(dabco) SURMOFs (Fig. 5.7 black, orange and violet).



Figure 5.7 Quartz crystal microbalance (QCM) uptake data for a series of metal compounds: Zn^{2+} (black), Ag^+ (red), Pd^{2+} (blue), Fe^{3+} (green), Cd^2 (orange)⁺, Ni⁺ (violet), Co^{2+} (wine).

5.1.3.4 Quantitative analysis of loading Fe^{3+} and Pd^{2+} into $Cu_2(atBDC)_2(dabco)$ SURMOF and $Cu_2(BDC)_2(dabco)$ SURMOF by QCM

As discussed above, the uptake capacities for Fe³⁺ and Pd²⁺ in Cu₂(atBDC)₂(dabco) SURMOF are 6 and 4 molecules per pore, respectively (Fig. 5.7 green and blue and Fig. 5.8, black). For comparison the Cu₂(BDC)₂(dabco) SURMOF exhibits much lower reactivity with an uptake capacity of 2 and 1 molecules per pore for Fe³⁺ and Pd²⁺ ions under the same conditions (Fig. 5.8, red). These results demonstrate that the sulfur and alkene functional groups in side-chains lead to a significant increase of the uptake capacity for metal ions. The diffusion coefficient of metal ions within SURMOFs can be calculated as described in detail in earlier publication.^[144] The calculated results show that the diffusion coefficient of Fe³⁺ in Cu₂(atBDC)₂(dabco) SURMOFs was 1.2 × 10^{-19} m²·s⁻¹ which are significantly lower than that in the Cu₂(BDC)₂(dabco) SURMOFs (1.3 × 10^{-18} m²s⁻¹) (Fig. 5.9 left). This means that the functionalized side-chain blocks the diffusion of Fe³⁺ into MOFs. The same phenomenon has also been observed for Pd²⁺ uptake. The diffusion coefficient are 2.1 × 10^{-19} m²·s⁻¹ and $1.0 × 10^{-18}$ m²·s⁻¹ for Pd²⁺ in Cu₂(atBDC)₂(dabco) SURMOF, respectively (Fig. 5.9 right).



Figure 5.8 Quartz crystal microbalance (QCM) uptake data of Fe^{3+} (left) and Pd^{2+} (right) for $Cu_2(atBDC)_2(dabco)$ (black) and $Cu_2(BDC)_2(dabco)$ (red).



Figure 5.9 Quartz crystal microbalance (QCM) uptake data of Fe^{3+} (left) and Pd^{2+} (right) for $Cu_2(atBDC)_2(dabco)$ (up) and $Cu_2(BDC)_2(dabco)$ (down).

5.1.3.5 Stability of the metal@ Cu₂(atBDC)₂(dabco) SURMOF by XRD

The stability of the $Cu_2(atBDC)_2(dabco)$ SURMOF after loading metal ions was measured upon immersing the sample in Fe³⁺ and Pd²⁺ solution for 3h (Fig. 5.10). The XRD data show that the intensity of the (001) peak has a significantly decrease for the loaded sample. One possible reason is that the places of guest metals are more close to the middle of the major pore and change the F-lattice into an I-lattice. The extinction rules for I-lattices lead to a decrease of the intensity. Another possible reason is the interaction of guest metals (Fe³⁺ and Pd²⁺) with dabco molecules is stronger than the intrinsic copper ions. The Fe³⁺ and Pd²⁺ ions may be able to enter and destroy a part of the SURMOF structure.



Figure 5.10 XRD patterns of $Cu_2(atBDC)_2(dabco)$ SURMOF (black), after loading $Fe(NO_3)_3$ (up red) and after loading $Pd(NO_3)_2$ (down red).

5.1.4 Conclusions

In this work, the Cu₂(atBDC)₂(dabco) SURMOFs grown on modified Au surface were successfully prepared as evidenced by XRD, IR and UV-Vis data. A series of metal ions uptake experiments by using the QCM to monitor mass change have been performed. The largest uptake capacity of Cu₂(atBDC)₂(dabco) SURMOF were obtained for Fe³⁺ and Pd²⁺ ions. Compared to the Cu₂(BDC)₂(dabco) SURMOF, we demonstrate that the side-chain of the Cu₂(atBDC)₂(dabco) SURMOF improves significantly the adsorption capacity for Fe³⁺ and Pd²⁺ ions. On the basis of the QCM data, the concentration of
loaded metal ions was determined to be 6 Fe^{3+} and 4 Pd^{2+} compounds per $\text{Cu}_2(\text{atBDC})_2(\text{dabco})$ SURMOF unit cell, respectively. In addition, a closer analysis of the uptake rates reveal that the diffusivity of guest molecules was enhanced to be $1.2 \times 10^{-19} \text{ m}^2 \cdot \text{s}^{-1}$ for Fe^{3+} and $2.1 \times 10^{-19} \text{ m}^2 \cdot \text{s}^{-1}$ for Pd^{2+} ions.

6 Loading metal ions into SURMOFs by using open metal sites as nucleation centers

Often neglected aspect of nucleation center in the MOF is the open coordination sites (OCSs) at metal centers. Among many of MOFs, OCSs at metal centers have been demonstrated to exhibit effective adsorption of small organic molecules (such as H₂O, NH₃ and CH₂Cl₂).^[89-91] In order to utilize these OCSs, choose a metal complex with small organic molecules which can effectively link with OCSs may be other approach to be considered. Here, we have loaded an metal-organic precious [Au(CO)Cl] into HKUST-1 SURMOFs by using gas-phase loading method and studied the reaction between [Au(CO)Cl] and the OCSs.

6.1 Au(CO)Cl gas-phase loading into HKUST-1 SURMOF

6.1.1 Background

Among many applications of MOFs, OCSs at the metal center have been demonstrated to play an important role. HKUST-1 is constructed of multiple units of Cu paddle-wheels coordinating four BTC linkers. In order to utilize these OCSs, an activation process has to be performed, e.g. to remove pre-coordinating solvent molecules (e.g. H_2O or EtOH) adsorbed at OCSs from the pores, which is a prerequisite step. In previous work, Raman and IR spectroscopy technologies were used to investigate the adsorption of small organic molecules, like dichloromethane, NH_3 and methane in MOFs.

In this work we report on a solvent-free gas-phase infiltration process to "chemically graft" Au(CO)Cl precursor via reaction with the per-coordinating solvent molecules (e.g. H₂O) at OCSs in the free and open pores of HKUST-1 SURMOFs (Fig. 6.1). As described below, we found that after loading Au(CO)Cl precursor into HKUST-1 SURMOF reactions between Au(CO)Cl and H₂O adsorbed at OCSs take place as evidenced by the observation of an active C=O bond and two new C=O and C-O bonds. In addition, we have observed unusual copper paddle-wheel structural changes on the basis of IR and Raman studies. This demonstrates the Au(CO)Cl "chemical graft" with the pre-coordinated H₂O at open Cu(II) sites paddle-wheel. The HKUST-1 SURMOF thin films chemically grafted with Au(CO)Cl, possess high electrical conductivity. Furthermore, we demonstrate that the Au(CO)Cl can be photo-degraded leading to the formation of large Au clusters in the metal organic framework.



Figure 6.1 (a) Synthesis scheme of AuClCO@HKUST-1 SURMOFs. (b) Illustration of "chemical graft" of the paddle-wheel Cu²⁺ node within HKUST-1 performed by AuClCO.

6.1.2 Preparation of the Au(CO)Cl@HKUST-1 SURMOF

All HKUST-1 SURMOFs used in the present work were grown on modified Au substrates, except the samples for the UV-vis, Tof-SIMS and XPS, which have been previously prepared on quartz glass or silicon substrates. The systemic method of SURMOF was described in section 1.3.2.2. Before further processing, all SURMOFs samples were characterized by XRD (Fig. 6.7 black).

The Au(CO)Cl@HKUST-1 SURMOF sample was prepared by using the gas-phase loading method. First a HKUST-1 SURMOF was placed into a 250 ml flask vessel, then, 1µg Au(CO)Cl powder was put quickly into the reaction flask and heated up to 80°C for 12h (Fig. 6.2). Subsequently, the sample was removed from the reaction flask and put into a sample box for later use. After loading all samples were characterized by XRD before further measurements.



Figure 6.2 Synthesis scheme of gas-phase loading method.

6.1.3 Results and discussion

6.1.3.1 SEM and ToF-SIMS analysis of the Au(CO)Cl@HKUST-1 SURMOF

The distribution of Au(CO)Cl molecules embedded into HKUST-1 SURMOFs was measured by the cross-sectional HR-SEM (Fig. 6.4). Since guest metals backscatter electrons more strongly than HKUST-1, the distribution of guest metals in SURMOFs can clearly be seen. Here, an HKUST-1 SURMOF with 45 layers was first loaded with Au(CO)Cl molecules, and then a thin (empty) HKUST-1 film (20 layers) was grown on the surface of the loaded SURMOF. The corresponding cross-sectional HR-SEM images show a well-defined confine between the loaded lower part of the SURMOF (45 layers Au(CO)Cl@HKUST-1) and the empty upper part (20 layers empty HKUST-1), demonstrating that the Au(CO)Cl molecules were uniformly dispersed inside the HKUST-1 SURMOF.



Figure 6.4 Scanning electron microscope (SEM) of 45 layers Au(CO)Cl@HKUST-1 + 20 layers pristine HKUST-1.

The same result has also been carried out from the ToF-SIMS data (Fig. 6.5). As shown in dynamic SIMS data, an additional Bi_3^+ beam was applied for erosion of a 450 × 450 μ m² field with a concentric analysis field of 250 × 250 μ m² (Fig. 6.5b). The results show compact and homogeneous Au atoms equally distributed in HKUST-1 thin films (Fig. 6.5c). Fig. 6.5a shows an intensity profile of Au⁺, Au³⁺, Cu²⁺ SiO²⁺ and Si⁺ from a 35 layers HKUST-1/Si wafer system. SiO²⁺ and Si⁺ signals result from continuous, compact and homogeneous Si wafer.



Figure 6.5 (a) Quasi-static SIMS of AuClCO@HKUST-1 SURMOF stack performed. (b) OM of AuClCO@HKUST-1 SURMOF before (up) and after (down) ToF-SIMS measurement. (c) The distribution of Au⁻, Au²⁻ atoms in AuClCO@HKUST-1 SURMOF.

6.1.3.2 XRD analysis of the Au(CO)Cl@HKUST-1 SURMOF

As mentioned above, HKUST-1 contains three types of different metal-organic cages (large, middle as well as small ones, Fig. 6.6). To its structural motifs, a face centered cubic close packing of the large cavity and middle cavity constructs HKUST-1 in (001) direction (Fig. 6.6a), whereby an alternating packing can be observed in the (111) direction (Fig. 6.6b). It is important to note that all OCSs face toward the open spaces of the large HKUST-1 cavity. Firstly, all OCSs possess mirror symmetry inside the large cavity of HKUST-1 along the (001) crystallographic direction (Fig. 6.6a). Secondly, the atomic spacing of percoordinating molecules (like H₂O) shows a significant overlap with the HKUST-1 lattice along the (111) crystallographic direction (Fig. 6.6b).



Figure 6.6 (a) Schematic illustration of distribution of OCSs in (001) crystallographic direction. (b) Schematic illustration of distribution of OCSs in (111) crystallographic direction.

The XRD data recorded in an out-of-plane geometry for the pristine, monolithic and oriented HKUST-1 SURMOFs are show in Fig. 6.7. As reported in previous works,^[74] the (002) and (004) peaks on MHDA-SAM and the (111) as well as the (222) peaks on MUD-SAM are well-defined and sharp, their relative intensities are in full agreement with our simulations, assuming high quality HKUST-1 thin films (Fig. 6.7, black). The absence of diffraction peaks for other crystallographic directions in the out-of-plane data reveals that the SURMOFs growth proceeds only along the (001) crystallographic direction on MHDA-SAM and the (111) crystallographic direction on MUD-SAM. The XRD data recorded after loading the Au(CO)Cl guest molecules into the HKUST-1 SURMOF (Fig. 6.7, red) do not affect the crystallinity of the host matrix. Although no additional new diffraction peaks have appeared, however, after loading Au(CO)Cl in the open MOF pores the ratio of the diffraction peak intensities have changed significantly. The (002)/(004) reflection ratio (out-of-plane data) from MHDA-SAM sample has significantly decreased from 1.76 for the pristine HKUST-1 SURMOF to near zero for the Au(CO)Cl loaded thin films (Fig. 6.7a). Also the in-plane XRD data show that the (200)/(400) ratio has dropped from 1.32 to near zero (Fig. 6.7c). For the MUD-SAM sample, the out-of-plane XRD data reveal pronounced changes: the reflection ratio of (111)/(222) has increased from 0.04 to 0.70 (Fig. 6.7b). Longer loading times did not lead to a further change of the relative XRD peak intensities.



Figure 6.7 X-ray diffraction patterns recorded: (a) Empty (black) and after loading AuCICO (red) HKUST-1 SURMOFs grown on a MHDA SAM modified Au substrates. (b) Empty (black) and after loading AuCICO (red) HKUST-1 SURMOFs grown on a MUD SAM modified Au substrates. (c) Empty (black), after loading AuCICO (red) and exposed UV-light 300 min (blue) of in-plane HKUST-1 SURMOF grown on a MHDA SAM modified Au substrates.

The same loading process has also been carried out for HKUST-1 powders for a comparison. The changes in relative peak intensities observed for the powders were similar to that seen for the SURMOFs (Fig. 6.8). The reflection ratio of (002)/(004) has dropped from 1.23 to near zero after loading Au(CO)Cl and the reflection ratio of (111)/(222) have thereby increased.



Figure 6.8 X-ray diffraction patterns recorded for empty (black), after loading AuClCO (red) and simulation (blue) of HKUST-1 powder.

This significant change in relative intensities of XRD-peaks directly demonstrates that Au⁺ are loaded in virtually every pore of the SURMOF as well as in MOF powders. A decoration of the outer surface only would not be compatible with the change of diffraction peak relative intensities.

In order to understand the experimental data and to further obtain detailed information regarding to the distinct positions of the precursor molecules within the MOF pores, we need to further evaluate the crystals structure factors of the pristine and the Au(CO)Cl loaded HKUST-1 SURMOFs. As reported in previous work,^[92] the structure factor directly affects the relative intensities of XRD-peaks under same conditions.

Since for reflections where F=0 the intensity is zero, these reflections cannot be observed in XRD and are called forbidden reflections.^[92] As shown in Fig.4.3.7a, for pristine HKUST-1 the structure factor of (002) reflective plane of is not zero, and XRD shows a well-defined and sharp (002) peak. However, after loading of Au(CO)Cl into HKUST-1 the (002) peak reflection has disappeared (Fig 6.7a). This means that the structure factor of (002) reflective plane decreases to be zero.

As described in more detail in section 2.1.2, we can calculate the structure factor of (002) reflective plane of Au(CO)Cl@HKUST-1 with:

$$\left|F_{(002)AuClCO@HKUST-1}\right|^{2} = \left[\sum_{j=1}^{48} f_{Cu_{j}}\cos 2\pi z_{j} + \sum_{m=1}^{n} f_{Au_{m}}\cos 2\pi z_{m}\right]^{2} + \left[\sum_{m=1}^{n} f_{Au_{m}}\sin 2\pi z_{m}\right]^{2} \approx 0$$

where f_{Cuj} represents the atomic scattering factor of the *j*-th Cu atom in the corresponding unit cell, f_{Aum} represents the atomic scattering factor of the *m*-th Au atom in the corresponding unit cell, and *z* represents the atomic coordinates in *z*-axis.

If the atoms in crystal lattice are mirror-symmetric, the value of $\sum_{m=1}^{n} f \sin 2\pi z_m$ will be equal to zero. For example, the atoms in pristine HKUST-1 are mirror-symmetric, so $\sum_{m=1}^{n} f_{Cu_m} \sin 2\pi z_m$ is equal to zero.

Since the (002) peak disappears after loading of Au(CO)Cl into HKUST-1, the value of $\sum_{m=1}^{n} f_{Au_m} \sin 2\pi z_m$ in equation (2) should be equal to zero. This suggests that the Au(CO)Cl molecular precursor are in a mirror symmetry inside the cavity of HKUST-1.

According to the experimental data, the (111) peak is very weak for the pristine HKUST-1 (Fig 6.7b). We therefore assume, that the structure factor of (111) reflective plane is almost equal to zero. We further calculated the structure factor of (111) reflective plane of Au(CO)Cl@HKUST-1 as follows:

$$\begin{split} \left| F_{(111)AuClCO@HKUST-1} \right|^2 &= \left[A_{(111)Cu} + A_{(111)Au} \right]^2 + \left[B_{(111)Cu} + B_{(111)Au} \right]^2 \\ &\approx \left[A_{(111)Au} \right]^2 + \left[B_{(111)Au} \right]^2 \\ A_{(111)Cu} &= \sum_{j=1}^{48} f_{Cu_j} \cos 2\pi (hx_j + ky_j + lz_j) \\ A_{(111)Au}^{'} &= \sum_{m=1}^{n} f_{Au_m} \cos 2\pi (hx_j + ky_j + lz_j) \\ B_{(111)Cu} &= \sum_{j=1}^{48} f_{Cu_j} \sin 2\pi (hx_j + ky_j + lz_j) \\ B_{(111)Au}^{'} &= \sum_{m=1}^{n} f_{Au_m} \sin 2\pi (hx_j + ky_j + lz_j) \end{split}$$

where *hkl* represents the crystallographic planes, *n* represents the total number of Au atoms in a unit cell, f_{Cuj} represents the atomic scattering factor of the *j*-th Cu atom in the corresponding unit cell, f_{Aum} represents the atomic scattering factor of the *m*-th Au atom in the corresponding unit cell, and (x, y, z) represents the atomic coordinates. According to previous reports,^[92] the atomic scattering factor for elements corresponds to the scattering amplitude of a wave by an isolated atom. The

atomic scattering factor depends on the incident radiation. Fig. 6.9 shows the atomic scattering factor curve for elements Cu and Au.



Figure 6.9 Atomic scattering factor curve for element Cu (left) and Au (right).

Therefore the main effect factor of the (111) peak intensity reflection is the distribution per Au atoms in the unit cell of HKUST-1. Considering the Bragg's law, the Bragg diffraction occurs when the radiation, with wavelength comparable to atomic spacing, is scattered in a specular fashion by the atoms of a crystalline system, and undergoes constructive interference. Therefore, we could assume that the atomic spacing of Au atoms is identical to the (111) reflective plane of the HKUST-1. By comparing the results and structure factor change, the most likely distribution of the Au(CO)Cl in HKUST-1 crystal lattice is related to the OCSs position.

6.1.3.3 Raman and IR analysis of the samples before and after Au(CO)CI loading

In order to further characterize the Au(CO)Cl "chemical graft" in the pores of HKUST-1 at the OCSs, we have carried out investigations using Raman spectroscopy. We postulate that the change in coordination around the Cu²⁺ centers would be reflected in the vibrational strength of the Cu-Cu bonding. As show in Fig. 6.10a, in the low-frequency region (600-179 cm⁻¹), the Raman spectrum of pristine HKUST-1 exhibits vibrational modes originating from Cu²⁺ species, especially stretching vibration modes of Cu-Cu bonding at 178 cm⁻¹ and 275 cm⁻¹ and the Cu-O stretching vibration at approximate 502 cm⁻¹. These assignments agree well with those previously reported for pristine HKUST-1,^[146] where the OCSs in HKUST-1 are coordinated with H₂O. A Raman shift of Cu-Cu bonding in AuClCO@HKUST-1 was detected at about 193 cm⁻¹ and 283 cm⁻¹ (Fig. 6.10a red), thus demonstrating that the coordination of OCSs in HKUST-1 has obviously changed. In addition, the Cu-O band at 502 cm⁻¹ does not show significant changes, suggesting that the copper paddle-wheel structure in HKUST-1 remains intact.



Figure 6.10 (a) Raman spectrum of empty (black) and after loading AuClCO (red) HKUST-1 SURMOFs. (b) IR spectrum of empty (black) andafter loading AuClCO (red) HKUST-1 SURMOFs.



Figure 6.11 IR spectrum for empty (black), after loading Au(CO)Cl (red) of HKUST-1 SURMOFs and Au(CO)Cl powder (blue).

AuCICO is a simple organo-gold compound which is a crystalline colorless solid. It is extremely moisture and temperature sensitive but is stable at room temperature. The AuCICO powder is characterized using IR by the intense C=O stretching vibration at 2160 cm⁻¹ (Fig. 6.11 blue).

The corresponding IR spectra are shown in Fig. 6.10b and Fig. 6.11. For the pristine HKUST-1 the intense bands at 1655 cm⁻¹ (COO⁻ asymmetric stretching), 1457 cm⁻¹ (COO⁻ symmetric stretching) and 1388 cm⁻¹ (COO⁻ symmetric stretching) are assigned to vibrations of COO⁻ in the framework (Fig. 6.10b black). After loading Au(CO)Cl into the HKUST-1 SURMOF, two new IR bands appear at 1728 and 1286 cm⁻¹ which are characteristic for C=O stretching vibration and C-O stretching vibration, respectively (Fig. 6.10b red). Au(CO)Cl is an extremely moisture sensitive chemical with an active C=O bond which can easily bind to H₂O.^[147] This means Au(CO)Cl reacts with the percoordinating H₂O in OCSs. It should be noted that the COO⁻ vibrations show slight shifts to lower frequencies (COO⁻ asymmetric stretching from 1655 cm⁻¹ to 1648 cm⁻¹; COO⁻ symmetric stretching from 1388 cm⁻¹ to 1380 cm⁻¹). This red-shift is also related to the change of coordination at OCSs. The present Raman and IR data reasonably support our primary postulate: Au(CO)Cl molecule can be "chemical grafted" by reaction with the precoordinated H₂O at OCSs of pristine HKUST-1.

6.1.3.4 Stability of the Au(CO)Cl@HKSUT-1 SURMOF by XRD

The stability of Au(CO)Cl@HKUST-1 under UV-light irradiation was investigated by XRD. The sample was exposed to 366 nm UV light in different time. The corresponding XRD data show a significant increase of (002) peak in intensity with increasing the exposed time (Fig. 6.12b). The (002)/(004) intensity ratio shows a large increase from zero to 0.88 (irradiation 300 min, Fig. 6.12b blue) and 1.51 (irradiation 1 day, Fig. 6.12b magenta). In addition, the change of the (002)/(004) intensity ratio is accompanied by a slight shift to smaller diffraction angles for both peaks, indicating a very slight (1.05%) expansion of the HKUST-1 unit cell. Since the intensity ratio and diffraction angle are clearly different for the parent HKUST-1, we propose that a photo-degradation process with the formation of large clusters in the metal organic framework occurs (Fig. 6.12a). Furthermore, the corresponding IR data show a gradual decrease in the intensity of the C=O stretching vibration at 1728 cm⁻¹ and the C-O stretching vibration at 1286 cm⁻¹ with the illumination time (Fig. 6.12c). More interesting is that the both COO⁻ vibrations at 1648 and 1380 cm⁻¹ show a slight back shift to higher frequencies.

The similar result is obtained by heating the Au(CO)Cl@HKUST-1 sample, as shown in Fig. 6.13. As the temperatures rise, the intensity ratio of the (002)/(004) reflections shows a fast increase until SURMOF has been destroyed upon heating to over 200 °C.



Figure 6.12 (a) Illustration of the photo-degradation process of AuClCO@HKUST-1 SURMOFs. (b) X-ray diffraction patterns recorded for empty (black), after loading AuClCO (red), exposed UV-light 300 min (blue) and exposed UV-light 1 day (magenta) of HKUST-1 SURMOFs. (c) IR spectrum for empty (black), after loading AuClCO (red), exposed UV-light 300 min (blue) and exposed UV-light 1 day (magenta) of HKUST-1 SURMOFs.



Figure 6.13 X-ray diffraction patterns recorded for heating on 30 °C (black), 70 °C (red), 110 °C (blue), 150 °C (magenta), 190 °C (dark yellow) and 230 °C (navy) of AuCICO@HKUST-1 SURMOFs.

6.1.4 Conclusions

We report on a novel synthesis strategy to chemically graft Au(CO)Cl with the precoordinated H_2O at open metal sites of HKUST-1 SURMOFs. The Au(CO)Cl@HKUST-1 hybrid materials have been prepared by a solvent-free gas-phase infiltration process, loading the molecular precursor Au(CO)Cl into the large cavity of a HKUST-1. We propose a plausible mechanism for this "chemical graft" process on the basis of XRD, Raman and IR investigations. We further demonstrate that the molecular Au(CO)Cl precursor is photo-degraded under UV irradiations leading to the formation of large Au clusters in the metal organic frameworks.

7 Conclusions

The primary objective of my dissertation is to explore the methodology of metal ion or NP loading into SURMOFs. SURMOF, such as HKUST-1, was grown in the form of thin, monolithic coatings on a modified Au substrate using LPE. LPE is a rather attractive method for depositing MOFs in layer-by-layer controlled manner, resulting in highly homogeneous, highly oriented, and crystalline MOF thin films. SURMOFs can be manufactured with thicknesses ranging from the nanometer regime up to the micrometer regime. SURMOFs facilitate the straightforward characterization of the optical, optoelectronic, mechanical, photonic, magnetic, electrical, and electrochemical properties of materials. In addition, SURMOFs provide a direct path for the fabrication of MOF-based membranes, which is of considerable interest for water purification. In this paper, the preparation, characterization, and application of metal@SURMOFs have been described in detail. The synthesized metal@SURMOFs were characterized by QCM, XRD, spectroscopic (IR, Raman, UV-Vis, ToF-SIMS) techniques, and microscopic (SEM and TEM) methods. Additionally, several important applications, such as photocatalysis or electrochemistry, have been introduced in this thesis.

The first methodology was described in Section 4, in which the nucleation centers originated from the main chain of ligands, usually the benzene ring. In Section 4.1, we presented a combined theoretical and experimental study on the loading of ionic compounds into MOFs. We used La³⁺ loading as an example to discuss the loading of metal ions in the open MOF framework. We demonstrated that La(OTf)₃ was successfully loaded into HKUST-1 SURMOF via solution impregnation method using XPS, ICP-OES, and IR measurements. Theoretical calculations using classical force field-based Monte Carlo simulations yielded a structure with two La³⁺ ions within the large HKUST-1 pores. This result is consistent with the experimental results on the composition of these films and the relative intensities of the XRD peaks.

Another example of the application of this method is discussed in Section 4.2. The Bi^{3+} ions were loaded into HKUST-1 SURMOF by the same process. The simulated and experimental XRD results have shown that three Bi^{3+} ions were successfully loaded into the pores of the HKUST-1 SURMOF. Moreover, the Bi_2O_3 nanoparticles encapsulated in SURMOF were obtained by photodecomposition of the Bi^{3+} precursors. The HKUST-1 SURMOF is an excellent template to provide a confined space that limits particle growth and impedes agglomeration. In this way, the dimension and shape of the Bi_2O_3 NPs, synthesized directly in the pores of the framework, should be controlled by pore size, shape, and channel structure of the

113

host material. The observed quantum-sized Bi_2O_3 semiconductor NPs (1–3 nm) possess enhanced photoefficiency. Therefore, the $Bi_2O_3@HKUST-1$ hybrid-system exhibits enhanced photocatalytic activity. The high photocatalytic activity of these heterostructures was demonstrated via the photodegradation of NFR dye.

The second methodology was described in Section 5. Highly oriented surface-anchored MOF thin films, in particular, $Cu_2(atBDC)_2(dabco)$, grown on the gold surface using LPE were successful prepared. A series of metal ion uptake experiments were performed using the QCM to monitor mass changes. According to the QCM data, the largest adsorption capacity of $Cu_2(atBDC)_2(dabco)$ SURMOFs was observed for Fe³⁺ and Pd²⁺ ions. Compared with the reference experiments of the $Cu_2(BDC)_2(dabco)$ SURMOF, we demonstrated that introducing sulfur and alkene side-chains into the ligands remarkably improved the adsorption ability of MOFs for Fe³⁺ and Pd²⁺ ions. However, we found that the functionalized side-chains could block the diffusion of metal ions into MOFs.

The last methodology was described in Section 6. Among the many applications of MOFs, OCSs at metal centers have been demonstrated to play an important role. An activation process was performed to remove pre-coordinating solvent molecules (e.g., H₂O or EtOH) adsorbed at the OCS from the pores, which is a prerequisite step to utilize these OCSs. In this study, we focused on the gas phase infiltration of Au(CO)Cl into the HKUST-1 SURMOFs. We demonstrated the chemical grafting of the precursor molecule Au(CO)Cl at OCSs in the open pores of HKUST-1. Au(CO)Cl coordinated to the free Cu(II) paddle-wheel sites yielding highly-conductive films. We further demonstrated that UV irradiation decomposed the chemically grafted Au(CO)Cl and led to the formation of larger Au clusters in the pores of HKUST-1.

List of abbreviations

1D	one-dimensional
2D	two-dimensional
3D	three-dimensional
AFM	Atomic force microscopy
atBDC	2,5-bis(allylthio)terephthalic acid
ATR	attenuated total reflection
Au(CO)Cl	chlorocarbonyl gold
BDC	terephthalic acid
Bi(Ph) ₃	triphenylbismuth
BTC	1,3,5-benzenetricarboxylic acid
СООН	carboxyl
Cu(OAc)	copper (II) acetate hydrate
dabco	1,4-Diazabicyclo [2.2.2] octane
DMF	dimethylformamide
ESI-MS	electrospray Ionization Mass Spectrometry
HKUST-1	Hong Kong University of Science and Technology-1
ICP-OES	inductively coupled plasma atomic emission spectroscopy
IR	infrared spectroscopy
IRRAS	infrared reflection-absorption spectroscopy
La(OTf) ₃	lanthanum(III) trifluoromethanesulfonate
LPE	liquid phase epitaxy
MHDA	16-mercaptohexadecanoic acid
MOF	metal organic frameworks
MUD	11-mercapto-1- undecanol
NFR	nuclear fast red
NPs	nanoparticles
ОН	hydroxyl
PP1	4-(4-pyridyl)phenyl)-methanethiol
QCM	quartz crystal microbalance
QCM-D	quartz crystal microbalance with dissipation monitoring
SAM	self-assembled monolayer
SBUs	secondary building units
SEM	scanning electron microscope
SURMOF	surface-mounted metal organic frameworks
TEM	transmission electron microscope

Tof-SIMS	time-of-flight secondary ion mass spectrometry
----------	--

- UV-Vis ultraviolet-visible spectroscopy
- XPS X-ray photoelectron spectroscopy
- XRD X-ray diffraction
- ZIF zeolitic imidazolate framework

References

- Banhart J: Manufacture, characterisation and application of cellular metals and metal foams. *Prog Mater Sci* 2001, 46(6):559-U553.
- 2. Zhang K, Han XP, Hu Z, Zhang XL, Tao ZL, Chen J: Nanostructured Mn-based oxides for electrochemical energy storage and conversion. *Chem Soc Rev* 2015, 44(3):699-728.
- Roberts AD, Li X, Zhang HF: Porous carbon spheres and monoliths: morphology control, pore size tuning and their applications as Li-ion battery anode materials. *Chem Soc Rev* 2014, 43(13):4341-4356.
- 4. Rowsell JLC, Yaghi OM: Metal-organic frameworks: a new class of porous materials. *Microporous Mesoporous Mat* 2004, 73(1-2):3-14.
- 5. Tao YS, Kanoh H, Abrams L, Kaneko K: Mesopore-modified zeolites: Preparation, characterization, and applications. *Chem Rev* 2006, 106(3):896-910.
- 6. Perego C, Millini R: Porous materials in catalysis: challenges for mesoporous materials. *Chem Soc Rev* 2013, 42(9):3956-3976.
- Kreno LE, Leong K, Farha OK, Allendorf M, Van Duyne RP, Hupp JT: Metal-Organic Framework Materials as Chemical Sensors. *Chem Rev* 2012, 112(2):1105-1125.
- Nugent P, Belmabkhout Y, Burd SD, Cairns AJ, Luebke R, Forrest K, Pham T, Ma SQ, Space B, Wojtas L et al: Porous materials with optimal adsorption thermodynamics and kinetics for CO2 separation. *Nature* 2013, 495(7439):80-84.
- 9. James SL: Metal-organic frameworks. *Chem Soc Rev* 2003, 32(5):276-288.
- 10. Zhou HC, Long JR, Yaghi OM: Introduction to Metal-Organic Frameworks. *Chem Rev* 2012, 112(2):673-674.
- 11. Kinoshita Y, Matsubara I, Higuchi T, Saito Y: The Crystal Structure of Bis(Adiponitrilo)Copper(I) Nitrate. *B Chem Soc Jpn* 1959, 32(11):1221-1226.
- 12. Mellot-Draznieks C, Dutour J, Ferey GR: Hybrid organic-inorganic frameworks: Routes for computational design and structure prediction. *Angew Chem-Int Edit* 2004, 43(46):6290-6296.
- 13. Makiura R, Motoyama S, Umemura Y, Yamanaka H, Sakata O, Kitagawa H: Surface nano-architecture of a metal-organic framework. *Nature Materials* 2010, 9(7):565-571.
- 14. Li H, Eddaoudi M, O'Keeffe M, Yaghi OM: Design and synthesis of an exceptionally stable and highly porous metal-organic framework. *Nature* 1999, 402(6759):276-279.
- 15. Lee J, Farha OK, Roberts J, Scheidt KA, Nguyen ST, Hupp JT: Metal-organic framework materials as catalysts. *Chem Soc Rev* 2009, 38(5):1450-1459.
- 16. Murray LJ, Dinca M, Long JR: Hydrogen storage in metal-organic frameworks. *Chem Soc Rev* 2009, 38(5):1294-1314.
- 17. Li JR, Sculley J, Zhou HC: Metal-Organic Frameworks for Separations. *Chem Rev* 2012, 112(2):869-932.
- 18. Eddaoudi M, Moler DB, Li HL, Chen BL, Reineke TM, O'Keeffe M, Yaghi OM: Modular chemistry: Secondary building units as a basis for the design of highly porous and robust metal-organic carboxylate frameworks. *Accounts of Chemical Research* 2001, 34(4):319-330.
- 19. Yaghi OM, Li GM, Li HL: Selective Binding and Removal of Guests in a Microporous Metal-Organic Framework. *Nature* 1995, 378(6558):703-706.

- 20. Tranchemontagne DJ, Mendoza-Cortes JL, O'Keeffe M, Yaghi OM: Secondary building units, nets and bonding in the chemistry of metal-organic frameworks. *Chem Soc Rev* 2009, 38(5):1257-1283.
- 21. Chui SSY, Lo SMF, Charmant JPH, Orpen AG, Williams ID: A chemically functionalizable nanoporous material [Cu₃(TMA)₂(H₂O)₃](n). *Science* 1999, 283(5405):1148-1150.
- Takei T, Ii T, Kawashima J, Ohmura T, Ichikawa M, Hosoe M, Shinya Y, Kanoya I, Mori W: Hydrogen-adsorption properties of a novel lantern-type dinuclear Co(BDC)(DABCO)_{1/2}. *Chem Lett* 2007, 36(9):1136-1137.
- Heck R, Shekhah O, Zybaylo O, Weidler PG, Friedrich F, Maul R, Wenzel W, Wöll C: Loading of Two Related Metal-Organic Frameworks (MOFs), [Cu₂(bdc)₂(dabco)] and [Cu₂(ndc)₂(dabco)], with Ferrocene. *Polymers-Basel* 2011, 3(3):1565-1574.
- 24. Liu J, Lukose B, Shekhah O, Arslan HK, Weidler P, Gliemann H, Braese S, Grosjean S, Godt A, Feng X et al: A novel series of isoreticular metal organic frameworks: realizing metastable structures by liquid phase epitaxy. *Sci Rep-Uk* 2012, 2.
- 25. He J, Zha MQ, Cui JS, Zeller M, Hunter AD, Yiu SM, Lee ST, Xu ZT: Convenient Detection of Pd(II) by a Metal-Organic Framework with Sulfur and Olefin Functions. *J Am Chem Soc* 2013, 135(21):7807-7810.
- 26. Eddaoudi M, Kim J, Rosi N, Vodak D, Wachter J, O'Keeffe M, Yaghi OM: Systematic design of pore size and functionality in isoreticular MOFs and their application in methane storage. *Science* 2002, 295(5554):469-472.
- 27. Ahrenholtz SR, Epley CC, Morris AJ: Solvothermal Preparation of an Electrocatalytic Metalloporphyrin MOF Thin Film and its Redox Hopping Charge-Transfer Mechanism. *J Am Chem Soc* 2014, 136(6):2464-2472.
- Bhattacharjee S, Choi JS, Yang ST, Choi SB, Kim J, Ahn WS: Solvothermal Synthesis of Fe-MOF-74 and Its Catalytic Properties in Phenol Hydroxylation. *J Nanosci Nanotechno* 2010, 10(1):135-141.
- 29. Qiu LG, Li ZQ, Wu Y, Wang W, Xu T, Jiang X: Facile synthesis of nanocrystals of a microporous metal-organic framework by an ultrasonic method and selective sensing of organoamines. *Chem Commun* 2008(31):3642-3644.
- 30. Hu SM, Niu HL, Qiu LG, Yuan YP, Jiang X, Xie AJ, Shen YH, Zhu JF: Facile synthesis of highly luminescent nanowires of a terbium-based metal-organic framework by an ultrasonic-assisted method and their application as a luminescent probe for selective sensing of organoamines. *Inorg Chem Commun* 2012, 17:147-150.
- 31. Khan NA, Haque E, Jhung SH: Rapid syntheses of a metal-organic framework material Cu-3(BTC)(2)(H2O)(3) under microwave: a quantitative analysis of accelerated syntheses. *Phys Chem Chem Phys* 2010, 12(11):2625-2631.
- 32. Yoo Y, Jeong HK: Rapid fabrication of metal organic framework thin films using microwave-induced thermal deposition. *Chem Commun* 2008(21):2441-2443.
- Joaristi AM, Juan-Alcaniz J, Serra-Crespo P, Kapteijn F, Gascon J: Electrochemical Synthesis of Some Archetypical Zn²⁺, Cu²⁺, and Al³⁺ Metal Organic Frameworks. *Cryst Growth Des* 2012, 12(7):3489-3498.
- 34. Singh NK, Hardi M, Balema VP: Mechanochemical synthesis of an yttrium based metal-organic framework. *Chem Commun* 2013, 49(10):972-974.
- 35. Matoga D, Oszajca M, Molenda M: Ground to conduct: mechanochemical synthesis of a

metal-organic framework with high proton conductivity. *Chem Commun* 2015, 51(36):7637-7640.

- Stock N, Biswas S: Synthesis of Metal-Organic Frameworks (MOFs): Routes to Various MOF Topologies, Morphologies, and Composites. *Chem Rev* 2012, 112(2):933-969.
- 37. Majano G, Perez-Ramirez J: Room Temperature Synthesis and Size Control of HKUST-1. *Helv Chim Acta* 2012, 95(11):2278-2286.
- 38. Rocio-Bautista P, Martinez-Benito C, Pino V, Pasan J, Ayala JH, Ruiz-Perez C, Afonso AM: The metal-organic framework HKUST-1 as efficient sorbent in a vortex-assisted dispersive micro solid-phase extraction of parabens from environmental waters, cosmetic creams, and human urine. *Talanta* 2015, 139:13-20.
- 39. Majano G, Martin O, Hammes M, Smeets S, Baerlocher C, Perez-Ramirez J: Solvent-Mediated Reconstruction of the Metal-Organic Framework HKUST-1 (Cu₃(BTC)₂). *Advanced functional materials* 2014, 24(25):3855-3865.
- 40. Ma DX, Li BY, Zhou XJ, Zhou Q, Liu K, Zeng G, Li GH, Shi Z, Feng SH: A dual functional MOF as a luminescent sensor for quantitatively detecting the concentration of nitrobenzene and temperature. *Chem Commun* 2013, 49(79):8964-8966.
- 41. Volkringer C, Loiseau T, Guillou N, Ferey G, Haouas M, Taulelle F, Elkaim E, Stock N: High-Throughput Aided Synthesis of the Porous Metal-Organic Framework-Type Aluminum Pyromellitate, MIL-121, with Extra Carboxylic Acid Functionalization. *Inorganic Chemistry* 2010, 49(21):9852-9862.
- 42. Choi JS, Son WJ, Kim J, Ahn WS: Metal-organic framework MOF-5 prepared by microwave heating: Factors to be considered. *Microporous Mesoporous Mat* 2008, 116(1-3):727-731.
- 43. Ubaid S, Zacharia R, Xiao J, Chahine R, Benard P, Tessier P: Effect of flowthrough cooling heat removal on the performances of MOF-5 cryo-adsorptive hydrogen reservoir for bulk storage applications. *Int J Hydrogen Energ* 2015, 40(30):9314-9325.
- Park KS, Ni Z, Cote AP, Choi JY, Huang RD, Uribe-Romo FJ, Chae HK, O'Keeffe M, Yaghi OM: Exceptional chemical and thermal stability of zeolitic imidazolate frameworks. *Proc Natl Acad Sci USA* 2006, 103(27):10186-10191.
- 45. Mason JA, Veenstra M, Long JR: Evaluating metal-organic frameworks for natural gas storage. *Chem Sci* 2014, 5(1):32-51.
- 46. Aguado S, Bergeret G, Titus MP, Moizan V, Nieto-Draghi C, Bats N, Farrusseng D: Guest-induced gate-opening of a zeolite imidazolate framework. *New J Chem* 2011, 35(3):546-550.
- 47. Ren JW, Langmi HW, North BC, Mathe M: Review on processing of metal-organic framework (MOF) materials towards system integration for hydrogen storage. *Int J Energ Res* 2015, 39(5):607-620.
- 48. Chang GG, Li B, Wang HL, Bao ZB, Yildirim T, Yao ZZ, Xiang SC, Zhou W, Chen BL: A microporous metal-organic framework with polarized trifluoromethyl groups for high methane storage. *Chem Commun* 2015, 51(79):14789-14792.
- Allen AJ, Espinal L, Wong-Ng W, Queen WL, Brown CM, Kline SR, Kauffman KL, Culp JT, Matranga C: Flexible metal-organic framework compounds: In situ studies for selective CO₂ capture. J Alloy Compd 2015, 647:24-34.
- 50. Peterson GW, Rossin JA, DeCoste JB, Killops KL, Browe M, Valdes E, Jones P: Zirconium Hydroxide-Metal-Organic Framework Composites for Toxic Chemical Removal. *Ind Eng Chem*

Res 2013, 52(15):5462-5469.

- 51. Wu CD, Hu A, Zhang L, Lin WB: Homochiral porous metal-organic framework for highly enantioselective heterogeneous asymmetric catalysis. *J Am Chem Soc* 2005, 127(25):8940-8941.
- 52. Douvali A, Tsipis AC, Eliseeva SV, Petoud S, Papaefstathiou GS, Malliakas CD, Papadas I, Armatas GS, Margiolaki I, Kanatzidis MG et al: Turn-On Luminescence Sensing and Real-Time Detection of Traces of Water in Organic Solvents by a Flexible Metal-Organic Framework. *Angew Chem-Int Edit* 2015, 54(5):1651-1656.
- 53. Etaiw SEH, Fouda AES, Amer SA, El-Bendary MM: Structure, Characterization and Anti-Corrosion Activity of the New Metal-Organic Framework [Ag(qox)(4-ab)]. *J Inorg Organomet P* 2011, 21(2):327-335.
- 54. He YB, Li B, O'Keeffe M, Chen BL: Multifunctional metal-organic frameworks constructed from meta-benzenedicarboxylate units. *Chem Soc Rev* 2014, 43(16):5618-5656.
- 55. Bradshaw D, Garai A, Huo J: Metal-organic framework growth at functional interfaces: thin films and composites for diverse applications. *Chem Soc Rev* 2012, 41(6):2344-2381.
- 56. Betard A, Fischer RA: Metal-Organic Framework Thin Films: From Fundamentals to Applications. *Chem Rev* 2012, 112(2):1055-1083.
- 57. Hermes S, Schroder F, Chelmowski R, Wöll C, Fischer RA: Selective nucleation and growth of metal-organic open framework thin films on patterned COOH/CF3-terminated self-assembled monolayers on Au(111). *J Am Chem Soc* 2005, 127(40):13744-13745.
- 58. Biemmi E, Scherb C, Bein T: Oriented growth of the metal organic framework Cu₃(BTC)₂(H₂O)₃ center dot xH₂O tunable with functionalized self-assembled monolayers. J Am Chem Soc 2007, 129(26):8054-+.
- 59. Shekhah O, Wang H, Zacher D, Fischer RA, Wöll C: Growth Mechanism of Metal-Organic Frameworks: Insights into the Nucleation by Employing a Step-by-Step Route. *Angew Chem-Int Edit* 2009, 48(27):5038-5041.
- 60. Shekhah O: Layer-by-Layer Method for the Synthesis and Growth of Surface Mounted Metal-Organic Frameworks (SURMOFs). *Materials* 2010, 3(2):1302-1315.
- 61. Ameloot R, Gobechiya E, Uji-i H, Martens JA, Hofkens J, Alaerts L, Sels BF, De Vos DE: Direct Patterning of Oriented Metal-Organic Framework Crystals via Control over Crystallization Kinetics in Clear Precursor Solutions. *Advanced Materials* 2010, 22(24):2685-+.
- 62. Horcajada P, Serre C, Grosso D, Boissiere C, Perruchas S, Sanchez C, Ferey G: Colloidal Route for Preparing Optical Thin Films of Nanoporous Metal-Organic Frameworks. *Advanced Materials* 2009, 21(19):1931-1935.
- 63. Ameloot R, Stappers L, Fransaer J, Alaerts L, Sels BF, De Vos DE: Patterned Growth of Metal-Organic Framework Coatings by Electrochemical Synthesis. *Chem Mat* 2009, 21(13):2580-2582.
- 64. Nan JP, Dong XL, Wang WJ, Jin WQ: Formation mechanism of metal-organic framework membranes derived from reactive seeding approach. *Microporous Mesoporous Mat* 2012, 155:90-98.
- 65. Schoedel A, Scherb C, Bein T: Oriented Nanoscale Films of Metal-Organic Frameworks By Room-Temperature Gel-Layer Synthesis. *Angew Chem-Int Edit* 2010, 49(40):7225-7228.
- 66. Tollner K, PopovitzBiro R, Lahav M, Milstein D: Impact of molecular order in Langmuir-Blodgett films on catalysis. *Science* 1997, 278(5346):2100-2102.

- 67. Heinke L, Cakici M, Dommaschk M, Grosjean S, Herges R, Brase S, Wöll C: Photoswitching in Two-Component Surface-Mounted Metal-Organic Frameworks: Optically Triggered Release from a Molecular Container. *Acs Nano* 2014, 8(2):1463-1467.
- Tu M, Wannapaiboon S, Fischer RA: Programmed functionalization of SURMOFs via liquid phase heteroepitaxial growth and post-synthetic modification. *Dalton T* 2013, 42(45):16029-16035.
- 69. Zybaylo O, Shekhah O, Wang H, Tafipolsky M, Schmid R, Johannsmann D, Wöll C: A novel method to measure diffusion coefficients in porous metal-organic frameworks. *Phys Chem Chem Phys* 2010, 12(28):8092-8097.
- 70. Tsotsalas M, Liu JX, Tettmann B, Grosjean S, Shahnas A, Wang ZB, Azucena C, Addicoat M, Heine T, Lahann J et al: Fabrication of Highly Uniform Gel Coatings by the Conversion of Surface-Anchored Metal-Organic Frameworks. J Am Chem Soc 2014, 136(1):8-11.
- 71. Lu G, Hupp JT: Metal-Organic Frameworks as Sensors: A ZIF-8 Based Fabry-Perot Device as a Selective Sensor for Chemical Vapors and Gases. *J Am Chem Soc* 2010, 132(23):7832-+.
- 72. Arnold R, Azzam W, Terfort A, Wöll C: Preparation, modification, and crystallinity of aliphatic and aromatic carboxylic acid terminated self-assembled monolayers. *Langmuir* 2002, 18(10):3980-3992.
- 73. Liu JX, Schupbach B, Bashir A, Shekhah O, Nefedov A, Kind M, Terfort A, Wöll C: Structural characterization of self-assembled monolayers of pyridine-terminated thiolates on gold. *Phys Chem Chem Phys* 2010, 12(17):4459-4472.
- 74. Arslan HK, Shekhah O, Wohlgemuth J, Franzreb M, Fischer RA, Wöll C: High-Throughput Fabrication of Uniform and Homogenous MOF Coatings. *Advanced functional materials* 2011, 21(22):4228-4231.
- Arslan HK, Shekhah O, Wieland DCF, Paulus M, Sternemann C, Schroer MA, Tiemeyer S, Tolan M, Fischer RA, Wöll C: Intercalation in Layered Metal-Organic Frameworks: Reversible Inclusion of an Extended pi-System. J Am Chem Soc 2011, 133(21):8158-8161.
- 76. Gu ZG, Pfriem A, Hamsch S, Breitwieser H, Wohlgemuth J, Heinke L, Gliemann H, Wöll C: Transparent films of metal-organic frameworks for optical applications. *Microporous Mesoporous Mat* 2015, 211:82-87.
- 77. Munuera C, Shekhah O, Wang H, Wöll C, Ocal C: The controlled growth of oriented metal-organic frameworks on functionalized surfaces as followed by scanning force microscopy. *Phys Chem Chem Phys* 2008, 10(48):7257-7261.
- 78. Wang C, deKrafft KE, Lin WB: Pt Nanoparticles@Photoactive Metal-Organic Frameworks: Efficient Hydrogen Evolution via Synergistic Photoexcitation and Electron Injection. J Am Chem Soc 2012, 134(17):7211-7214.
- 79. Jiang HL, Liu B, Akita T, Haruta M, Sakurai H, Xu Q: Au@ZIF-8: CO Oxidation over Gold Nanoparticles Deposited to Metal-Organic Framework. J Am Chem Soc 2009, 131(32):11302-+.
- 80. Gao JK, Miao JW, Li PZ, Teng WY, Yang L, Zhao YL, Liu B, Zhang QC: A p-type Ti(IV)-based metal-organic framework with visible-light photo-response. *Chem Commun* 2014, 50(29):3786-3788.
- 81. Guo W, Liu JX, Weidler PG, Liu JX, Neumann T, Danilov D, Wenzel W, Feldmann C, Wöll C: Loading of ionic compounds into metal-organic frameworks: a joint theoretical and experimental study for the case of La³⁺. *Phys Chem Chem Phys* 2014, 16(33):17918-17923.

- 82. Srinivasan NB, Thiede TB, de los Arcos T, Gwildies V, Krasnopolski M, Becker HW, Rogalla D, Devi A, Fischer RA: Transition metal nitride thin films grown by MOCVD using amidinato based complexes [M((NBu)-Bu-t)₂{((PrN)-Pr-i)₂CMe}₂] (M = Mo, W) as precursors. Surface & Coatings Technology 2013, 230:130-136.
- 83. Liang Q, Zhao Z, Liu J, Wei YC, Jiang GY, Duan AJ: Pd Nanoparticles Deposited on Metal-Organic Framework of MIL-53(Al): an Active Catalyst for CO Oxidation. *Acta Phys-Chim Sin* 2014, 30(1):129-134.
- Peters AW, Li ZY, Farha OK, Hupp JT: Atomically Precise Growth of Catalytically Active Cobalt Sulfide on Flat Surfaces and within a Metal-Organic Framework via Atomic Layer Deposition. Acs Nano 2015, 9(8):8484-8490.
- Heinke L, Wöll C: Adsorption and diffusion in thin films of nanoporous metal-organic frameworks: ferrocene in SURMOF Cu₂(ndc)₂(dabco). *Phys Chem Chem Phys* 2013, 15(23):9295-9299.
- 86. Dhakshinamoorthy A, Garcia H: Catalysis by metal nanoparticles embedded on metal-organic frameworks. *Chem Soc Rev* 2012, 41(15):5262-5284.
- 87. Gu ZG, Fu H, Neumann T, Xu ZX, Fu WQ, Wenzel W, Zhang L, Zhang J, Wöll C: Chiral Porous Metacrystals: Employing Liquid-Phase Epitaxy to Assemble Enantiopure Metal–Organic Nanoclusters into Molecular Framework Pores. *Acs Nano* 2015.
- Guo W, Liu JX, Weidler PG, Liu JX, Neumann T, Danilov D, Wenzel W, Feldmann C, Wöll C: Loading of ionic compounds into metal-organic frameworks: a joint theoretical and experimental study for the case of La³⁺. *Phys Chem Chem Phys* 2014, 16(33):17918-17923.
- Borfecchia E, Maurelli S, Gianolio D, Groppo E, Chiesa M, Bonino F, Lamberti C: Insights into Adsorption of NH3 on HKUST-1 Metal-Organic Framework: A Multitechnique Approach. J Phys Chem C 2012, 116(37):19839-19850.
- 90. Kim HK, Yun WS, Kim MB, Kim JY, Bae YS, Lee J, Jeong NC: A Chemical Route to Activation of Open Metal Sites in the Copper-Based Metal-Organic Framework Materials HKUST-1 and Cu-MOF2. J Am Chem Soc 2015, 137(31):10009-10015.
- 91. Getzschmann J, Senkovska I, Wallacher D, Tovar M, Fairen-Jimenez D, Duren T, van Baten JM, Krishna R, Kaskel S: Methane storage mechanism in the metal-organic framework Cu₃(btc)₂: An in situ neutron diffraction study. *Microporous Mesoporous Mat* 2010, 136(1-3):50-58.
- 92. Yoshio W, Eiichiro M, Kozo S: X-Ray Diffraction Crystallography: Introduction, Examples and Solved Problems. *Springer* 2011:67-167.
- 93. Peter L: IR and Raman spectroscopy: priciples and spectral interpretation. *Elsevier Inc* 2011:1-217.
- 94. Kattner J, Hoffman H: External reflection spectroscopy of thin films on dielectric substrates. Handbook of Vibrational Spectroscopy 2002:1-16.
- 95. Bruker Company. https://wwwbrukercom/products/infrared-near-infrared-and-ramanspectroscopy/ftir-research-spectrometers/vertex-series/vertex-7070v 2015.
- 96. Mojet BL, Ebbesen SD, Lefferts L: Light at the interface: the potential of attenuated total reflection infrared spectroscopy for understanding heterogeneous catalysis in water. *Chem Soc Rev* 2010, 39(12):4643-4655.
- 97. Wikipedia. *https://enwikipediaorg/wiki/Ultraviolet%E2%80%93visible_spectroscopy* 2015.
- 98. Wikipedia. https://enwikipediaorg/wiki/X-ray_photoelectron_spectroscopy 2015.
- 99. Chemistry in Britain. http://wwwrscorg/chemistryworld/Issues/2003/February/togetherasp

2015.

- 100. Henry G: Elemental Analyses by ICP-AES. Perkin-Elemer company, www.unn.ru/chem/ism /files/applecture21(2).pdf. 2008
- 101. University of Goettingen. http://www.geobiologie.uni-goettingen.de/people/vthiel/tof_sims /index_e.shtml. 2015.
- 102. howstuffworks citation. *http://science.howstuffworks.com/scanning-electron-microscope2. htm*. 2015.
- 103. Haugstad G: Atomic Force Microscopy: Understanding Basic Modes and Advanced Applications. *Wiley* 2012, Hoboken.
- 104. Wikipedia. https://simple.wikipedia.org/wiki/Atomic_force_microscope. 2015.
- 105. hk-phy. http://www.hk-phy.org/atomic_world/tem/tem02_e.html. 2015.
- 106. Lyshevski SE: Dekker Encyclopedia of Nanoscience and Nanotechnology. Third Edition, Seven Volume Set. 2014:6290.
- 107. Heinke L, Gu ZG, Wöll C: The surface barrier phenomenon at the loading of metal-organic frameworks. *Nat Commun* 2014, 5.
- 108. Alvaro M, Carbonell E, Ferrer B, Xamena FXLI, Garcia H: Semiconductor behavior of a metal-organic framework (MOF). *Chemistry-a European Journal* 2007, 13(18):5106-5112.
- 109. Tachikawa T, Choi JR, Fujitsuka M, Majima T: Photoinduced charge-transfer processes on MOF-5 nanoparticles: Elucidating differences between metal-organic frameworks and semiconductor metal oxides. *J Phys Chem C* 2008, 112(36):14090-14101.
- 110. Morrison SR: Electrochemistry at semiconductor and oxidized metal electrodes. *Plenum Publishing Corporation* 1980:1-407.
- 111. Silvestre ME, Franzreb M, Weidler PG, Shekhah O, Wöll C: Magnetic Cores with Porous Coatings: Growth of Metal-Organic Frameworks on Particles Using Liquid Phase Epitaxy. *Advanced functional materials* 2013, 23(9):1210-1213.
- 112. Gu ZG, Pfriem A, Hamsch S, Breitwieser H, Wohlgemuth J, Heinke L, Gliemann H, Wöll C: Transparent films of metal-organic frameworks for optical applications. *Microporous Mesoporous Mat* 2015, 211:82-87.
- 113. Strunk T, Wolf M, Brieg M, Klenin K, Biewer A, Tristram F, Ernst M, Kleine PJ, Heilmann N, Kondov I et al: SIMONA 1.0: An efficient and versatile framework for stochastic simulations of molecular and nanoscale systems. *J Comput Chem* 2012, 33(32):2602-2613.
- 114. Kirkpatrick S, Gelatt CD, Vecchi MP: Optimization by Simulated Annealing. *Science* 1983, 220(4598):671-680.
- 115. Li ZQ, Scheraga HA: Monte-Carlo-Minimization Approach to the Multiple-Minima Problem in Protein Folding. *Proc Natl Acad Sci USA* 1987, 84(19):6611-6615.
- 116. Wales DJ, Scheraga HA: Review: Chemistry Global optimization of clusters, crystals, and biomolecules. *Science* 1999, 285(5432):1368-1372.
- 117. Ahlrichs R, Bar M, Haser M, Horn H, Kolmel C: Electronic-Structure Calculations on Workstation Computers the Program System Turbomole. *Chemical Physics Letters* 1989, 162(3):165-169.
- 118. Esken D, Turner S, Lebedev OI, Van Tendeloo G, Fischer RA: Au@ZIFs: Stabilization and Encapsulation of Cavity-Size Matching Gold Clusters inside Functionalized Zeolite Imidazolate Frameworks, ZIFs. *Chem Mat* 2010, 22(23):6393-6401.
- 119. Esken D, Noei H, Wang YM, Wiktor C, Turner S, Van Tendeloo G, Fischer RA: ZnO@ZIF-8:

stabilization of quantum confined ZnO nanoparticles by a zinc methylimidazolate framework and their surface structural characterization probed by CO₂ adsorption. *J Mater Chem* 2011, 21(16):5907-5915.

- 120. Esken D, Zhang X, Lebedev OI, Schroder F, Fischer RA: Pd@MOF-5: limitations of gas-phase infiltration and solution impregnation of $[Zn_4O(bdc)_3]$ (MOF-5) with metal-organic palladium precursors for loading with Pd nanoparticles. *J Mater Chem* 2009, 19(9):1314-1319.
- 121. Yang SJ, Cho JH, Nahm KS, Park CR: Enhanced hydrogen storage capacity of Pt-loaded CNT@MOF-5 hybrid composites. *Int J Hydrogen Energ* 2010, 35(23):13062-13067.
- 122. Proch S, Herrmannsdorfer J, Kempe R, Kern C, Jess A, Seyfarth L, Senker J: Pt@MOF-177: Synthesis, Room-Temperature Hydrogen Storage and Oxidation Catalysis. *Chemistry-a European Journal* 2008, 14(27):8204-8212.
- 123. Ye JY, Liu CJ: $Cu_3(BTC)_2$: CO oxidation over MOF based catalysts. *Chem Commun* 2011, 47(7):2167-2169.
- 124. Ishida T, Nagaoka M, Akita T, Haruta M: Deposition of Gold Clusters on Porous Coordination Polymers by Solid Grinding and Their Catalytic Activity in Aerobic Oxidation of Alcohols. *Chemistry-a European Journal* 2008, 14(28):8456-8460.
- 125. Zybaylo O, Shekhah O, Wang H, Tafipolsky M, Schmid R, Johannsmann D, Wöll C: A novel method to measure diffusion coefficients in porous metal-organic frameworks. *Phys Chem Chem Phys* 2010, 12(28):8092-8097.
- 126. Atuchin VV, Kalinkin AV, Kochubey VA, Kruchinin VN, Vemuri RS, Ramana CV: Spectroscopic ellipsometry and x-ray photoelectron spectroscopy of La₂O₃ thin films deposited by reactive magnetron sputtering. *J Vac Sci Technol A* 2011, 29(2).
- 127. Ravelli D, Dondi D, Fagnoni M, Albini A: Photocatalysis. A multi-faceted concept for green chemistry. *Chem Soc Rev* 2009, 38(7):1999-2011.
- 128. Ke DN, Peng TY, Ma L, Cai P, Jiang P: Photocatalytic water splitting for O₂ production under visible-light irradiation on BiVO₄ nanoparticles in different sacrificial reagent solutions. *Appl Catal a-Gen* 2008, 350(1):111-117.
- 129. Pullen S, Fei HH, Orthaber A, Cohen SM, Ott S: Enhanced Photochemical Hydrogen Production by a Molecular Diiron Catalyst Incorporated into a Metal-Organic Framework. *J Am Chem Soc* 2013, 135(45):16997-17003.
- 130. Steinke T, Gemel C, Winter M, Fischer RA: [Pd₃(InCp*)₄(mu₂-InCp*)(4)]: Three linearly arranged palladium atoms wrapped into a fluxional shell of eight InCp* ligands. *Angew Chem-Int Edit* 2002, 41(24):4761-4763.
- 131. Wu PY, He C, Wang J, Peng XJ, Li XZ, An YL, Duan CY: Photoactive Chiral Metal-Organic Frameworks for Light-Driven Asymmetric alpha-Alkylation of Aldehydes. *J Am Chem Soc* 2012, 134(36):14991-14999.
- 132. Berger RJF, Rettenwander D, Spirk S, Wolf C, Patzschke M, Ertl M, Monkowius U, Mitzel NW: Relativistic effects in triphenylbismuth and their influence on molecular structure and spectroscopic properties. *Phys Chem Chem Phys* 2012, 14(44):15520-15524.
- Zhang LS, Wang WZ, Yang JO, Chen ZG, Zhang WQ, Zhou L, Liu SW: Sonochemical synthesis of nanocrystallite Bi₂O₃ as a visible-light-driven photocatalyst. *Appl Catal a-Gen* 2006, 308:105-110.
- 134. Streit HC, Adlung M, Shekhah O, Stammer X, Arslan HK, Zybaylo O, Ladnorg T, Gliemann H, Franzreb M, Wöll C et al: Surface-Anchored MOF-Based Photonic Antennae. *ChemPhysChem*

2012, 13(11):2699-2702.

- 135. Geudtner G, Calaminici P, Koster AM: Growth Pattern of (Bi₂O₃)_n Clusters with n=1-5: A First Principle Investigation. *J Phys Chem C* 2013, 117(25):13210-13216.
- 136. Fielicke A, Rademann K: Interaction of bismuth oxide cluster cations with alkenes and molecular oxygen: $Bi_4O_6^+$, a possible reactive center for alkene oxidation. *J Phys Chem A* 2000, 104(30):6979-6982.
- 137. Horcajada P, Gref R, Baati T, Allan PK, Maurin G, Couvreur P, Ferey G, Morris RE, Serre C: Metal-Organic Frameworks in Biomedicine. *Chem Rev* 2012, 112(2):1232-1268.
- 138. Qiu SL, Xue M, Zhu GS: Metal-organic framework membranes: from synthesis to separation application. *Chem Soc Rev* 2014, 43(16):6116-6140.
- 139. Zhang YW, Li Z, Zhao Q, Zhou YL, Liu HW, Zhang XX: A facilely synthesized amino-functionalized metal-organic framework for highly specific and efficient enrichment of glycopeptides. *Chem Commun* 2014, 50(78):11504-11506.
- 140. Tsotsalas M, Liu JX, Tettmann B, Grosjean S, Shahnas A, Wang ZB, Azucena C, Addicoat M, Heine T, Lahann J et al: Fabrication of Highly Uniform Gel Coatings by the Conversion of Surface-Anchored Metal-Organic Frameworks. J Am Chem Soc 2014, 136(1):8-11.
- Phang WJ, Jo H, Lee WR, Song JH, Yoo K, Kim B, Hong CS: Superprotonic Conductivity of a UiO-66 Framework Functionalized with Sulfonic Acid Groups by Facile Postsynthetic Oxidation. *Angew Chem-Int Edit* 2015, 54(17):5142-5146.
- 142. Sun L, Miyakai T, Seki S, Dinca M: Mn₂(2,5-disulfhydrylbenzene-1,4-dicarboxylate): A Microporous Metal-Organic Framework with Infinite (-Mn-S-)(infinity) Chains and High Intrinsic Charge Mobility. J Am Chem Soc 2013, 135(22):8185-8188.
- 143. Bhattacharjee S, Lee YR, Puthiaraj P, Cho SM, Ahn WS: Metal-Organic Frameworks for Catalysis. *Catal Surv Asia* 2015, 19(4):203-222.
- 144. Zybaylo O, Shekhah O, Wang H, Tafipolsky M, Schmid R, Johannsmann D, Wöll C: A novel method to measure diffusion coefficients in porous metal-organic frameworks. *Phys Chem Chem Phys* 2010, 12(28):8092-8097.
- 145. Nguyen TT, Phan NTS: A Metal-Organic Framework Cu₂(BDC)₂(DABCO) as an Efficient and Reusable Catalyst for Ullmann-Type N-Arylation of Imidazoles. *Catal Lett* 2014, 144(11):1877-1883.
- 146. Prestipino C, Regli L, Vitillo JG, Bonino F, Damin A, Lamberti C, Zecchina A, Solari PL, Kongshaug KO, Bordiga S: Local structure of framework Cu(II) in HKUST-1 metallorganic framework: Spectroscopic characterization upon activation and interaction with adsorbates. *Chem Mat* 2006, 18(5):1337-1346.
- 147. Antes I, Dapprich S, Frenking G, Schwerdtfeger P: Stability of group 11 carbonyl complexes Cl-M-CO (M=Cu,Ag,Au). *Inorganic Chemistry* 1996, 35(7):2089-2096.

Publications

- <u>W. Guo</u>, J. X. Liu, P. G. Weidler, J. X. Liu, T. Neumann, D. Danilov, W. Wenzel, C. Feldmann and C. Wöll: Loading of ionic compounds into metal-organic frameworks: a joint theoretical and experimental study for the case of La³⁺. *Phys Chem Chem Phys* 2014, **16**(33):17918-17923.
- Z. B. Wang, D. Nminibapied, P. Shrestha, J. X. Liu, <u>W. Guo</u>, P. G. Weidler, H. Baumgart, C. Wöll, E. Redel: Resistive Switching Nanodevices Based on Metal–Organic Frameworks. *Chem Nano Mat* 2015, 00(0-0):1-7.
- Z. B. Wang, J. X. Liu, S. Grosjean, D. Wagner, <u>W. Guo</u>, Z. G. Gu, L. Heinke, H. Gliemann, S. Brase, C. Wöll, E. Redel: Monolithic, Crystalline MOF Coating: AnExcellent Patterning and Photoresist Material. *Chem Nano Mat* 2015, 1:338-345.
- <u>W. Guo</u>, C. Zhi, C. W. Yang, T. Neumann, C. Kübel, W. Wenzel, A. Welle, W. Pfleging,
 O. Shekhah, C. Wöll and E. Redel: Bi₂O₃ nanoparticles encapsulated in surface mounted metal-organic frameworks. *Nanoscale* 2016, Accepted Manuscript.
- <u>W. Guo</u>, P. G. Weidler, X. J. Yu, A. Welle, S. Heissler, T. Neumann, Y. M. Wang, W. Wenzel, C. Wöll and E. Redel: Formation of highly conductive SURMOF thin films by grafting Au(CO)Cl with pre-coordinated H₂O in open metal sites of HKUST-1 pores. Submitted.
- 6. <u>W. Guo</u>, C. Wöll: Quantitative analysis of metal ions adsorption in functionalized Metal organic frameworks with sulfur and alkene side-chain. **To be submitted.**

Acknowledgments

First of all, I would like to thank my supervisor, Prof. Dr. Christof Wöll, for giving me many interesting projects and offering extremely helpful suggestions and encouragement during my PhD study. I really appreciate the time and effort he contributed to my study. All of the help have been of inestimable worth to the completion of my thesis.

I would like to thank Prof. Dr. Stefan Bräse for the co-referee in my thesis.

I would like to thank Dr. Hartmut Gliemann and Dr. Peter Weidler for his help during my Ph.D study in IFG. He endlessly encouraged and supported my project during these three years.

I would like to thank Dr. Engelbert Redel give me continuously guidance of my work during Ph.D study, in particular many helps and learn for how to start the project. He continuously gives the advice on the writing of paper and PhD thesis.

I would like to thank Peter Krolla-Sidenstein and Stefan Heissler for offering me the training of characterization methods and also for a lot of helpful measurement.

I would like to thanks to other IFG colleagues, Dr. Zhigang Gu, Dr. Zhengbang Wang, Weiwei, Qin, Jianxi Liu, Chengwu Yang, Wencai Zhou, Peter Lindemann, Dr. Manuel Tsotsalas, Dr. Lars Heinke and Sophia Schmitt for their help in my work and live.

I would like to thank the cooperative group Prof. Dr. Claus Feldmann for providing me the organic chemicals. Without her help

I would like to thank the cooperative group Prof. Dr. Wolfgang Wenzel, Dr. Denis Danilov and Tobias Neumann for their theoretical analysis in Institute of Nanotechnologie (INT) at KIT. Their efforts help me to improvement of my results.

I would like to thanks all the support staff of Faculty of Chemistry and Bioscience and the secretaries of IFG for all the documents during my PhD study.

I would like to thanks to my Master supervisor, Prof. Dr. Haolin Tang, for guide me beginning scientific studies.

I would like to express my gratitude to my parents and other family members for their constant support and endless love.

Finally, I would like to thanks of the China Scholarship Council and Deutsche Forschungsgemeinschaft (DFG) within the Priority Program Metal–Organic Frameworks for providing the financial support for this PHD study.